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**Fast Plasma Mixing:  
A New Excitation Method for CW Gas Lasers**

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**G. Schaefer  
and  
H. Kirkici**

**March 15, 1990**

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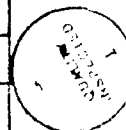
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## Table of Contents

ABSTRACT		1
I. INTRODUCTION		2
II. DEVICE DEVELOPMENT		3
I.1 Flowing Hollow Cathode Device		3
I.2 Constricted Arc Device		5
III. INVESTIGATIONS OF ENERGY AND CHARGE TRANSFER PROCESSES		6
III.1 Excited Atoms - Dissociative Excitation		6
III.2 Excited Molecules and Molecular Ions		8
III.3 Excimer Generation - Rare Gas Halides		10
IV. CONCLUSION		13
V. REFERENCES		13
APPENDIX I		15
APPENDIX II		19
APPENDIX III		42
APPENDIX IV		48

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## ABSTRACT

Resonant and near resonant energy and charge transfer collisions to molecules are effective mechanisms to generate population inversions in gas lasers. A new technique (fast plasma mixing) has been developed in which metastables and ions are generated separately in a flowing plasma source and then mixed with a molecular beam. Two CW systems, based on a flowing hollow cathode and a constricted arc have been designed. Experiments with several molecular systems have demonstrated selective excitation of atoms, molecules, molecular ions, and excimers. Spectroscopic investigations allowed determining branching ratios and the geometric distribution of the excitation in the mixing volume. CW laser action was achieved in oxygen and fluorine and experiments were performed to clarify the excitation mechanisms. First experiments on ArF and KrF excimer generation were performed and the fluorescence profiles were investigated depending on operating parameters.

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## I. INTRODUCTION

The research under the previous contract has concentrated on the development, analysis, and optimization of plasma mixing devices, and investigations of energy transfer collisions in different systems and their utilization for the operation as lasers.

Resonant or near resonant energy transfer from metastable rare gas atoms to other species have, from the beginning of gas laser development, been recognized as an ideal mechanism to generate population inversions for laser action in the near-IR, visible and near-UV spectral regime [1]. The major advantage of this mechanism is that only a small number of states (the upper laser states) are excited and that essentially no atoms are directly excited into the lower laser states.

The disadvantage of this mechanism comes from the fact that the metastable atoms have to be produced first and that at the same time a sufficient density of collision partners in the ground state has to be maintained. This is usually accomplished either in an externally sustained plasma or in a gas discharge in a mixture of a rare gas in which the metastables are produced and a second gas to which the energy transfer process into highly excited states takes place. This second gas, therefore, has energy states with excitation cross sections with much lower threshold energies than the rare gas. If the plasma is sustained by an external high energy electron beam, then the efficiency of producing metastable rare gas atoms only depends on the values of the cross sections at high energies and not on the differences in the threshold energy. In a gas discharge, however, the low energy electrons generated through ionization have to be accelerated in the gas before they can excite and subsequently they lose their energy again in the inelastic (and elastic) collisions. Excitation of the atoms with the lower excitation threshold therefore has a much higher probability.

An additional advantage can be gained by utilizing near resonant energy transfer collisions between metastable rare gas atoms and molecules. The quantum efficiency in molecular systems can be much higher because of the high density of low lying vibrational and rotational states in the electronic ground state which can act as the lower laser states. However, two disadvantages result from using molecules. The first disadvantage is that near resonant energy transfer now can lead to a large number of energy states or even into a band, and consequently the gain of the laser is lower. This problem does not occur if the molecules are excited into a repulsive branch and dissociate into fragments, one of which is an excited atom. In this case, of course, also the advantage of a possible high quantum efficiency is lost. The other disadvantage is that the high density of low lying states in molecules makes it nearly impossible to generate metastable rare gas atoms efficiently in gas discharges unless the fraction of the molecular gas is very low ( $\leq 10^{-3}$ ).

As an alternative excitation method for utilizing near resonant energy and charge transfer from metastable rare gas atoms to molecules we, therefore, proposed to use fast plasma mixing of two beams, one containing metastable rare gas atoms and/or ions at high densities, and the other containing the molecular species [2].

Besides the advantages mentioned above, this method also provides significant insight into the excitation mechanisms of lasers excited by energy transfer collisions. In a gas discharge other mechanisms compete based on the direct interaction of fast electrons with the molecular gas. Such processes may not play a significant role if the plasma generation is well separated from the mixing regime where the excitation through energy transfer occurs.

Another advantage of this method comes from the contribution of a fast flow and a small excitation volume. Many lasers have excitation mechanisms which start with molecular species and end up with atomic species. In a stationary gas, the laser is terminated when the density of starting molecules are depleted. Typical examples are the rare gas-halide excimer lasers [14]. A fast gas exchange can provide operating conditions for continuous excimer generation.

## II. DEVICE DEVELOPMENT

Two different types of plasma mixing devices have been developed, one based on a flowing hollow cathode discharge and one based on a constricted arc (Fig. 1). The properties of these two devices are significantly different and both have their advantages and disadvantages.

### II.1 Flowing Hollow Cathode Device

The flowing hollow cathode device generates the plasma in a slit-hollow cathode which acts, at the same time, as the nozzle for the plasma jet. The hollow cathode cross section was typically 0.1mm x 20mm and the length (in flow direction) was 1-2mm. Single and dual side flow (Fig. 1) was investigated. Optimum conditions for hollow cathode operation are in the regime  $10 \text{ mbar mm} \leq pd \leq 100 \text{ mbar mm}$ , here  $p$  is the pressure and  $d$  is the slit width. At a slit of 0.1 mm, we expect optimum conditions at pressures of  $100 \text{ mbar} \leq p \leq 1000 \text{ mbar}$ . The optimum outlet pressure was, for most investigated gas combinations, lower than 100 mbar. As a consequence, the active part of the hollow cathode was the upstream part of the slit. The generated plasma, on its path to the nozzle exit, has sufficient time for the relaxation of the electron energy distribution and no high energy electrons at significant densities are expected to reach the mixing zone. As a result, all excitation processes in the mixing zone have to be the result of energy and charge transfer collisions which makes it much easier to analyze the fluorescence spectra from the mixing zone. The disadvantage of this system is the limited density of metastables and ions in the plasma beam [3].

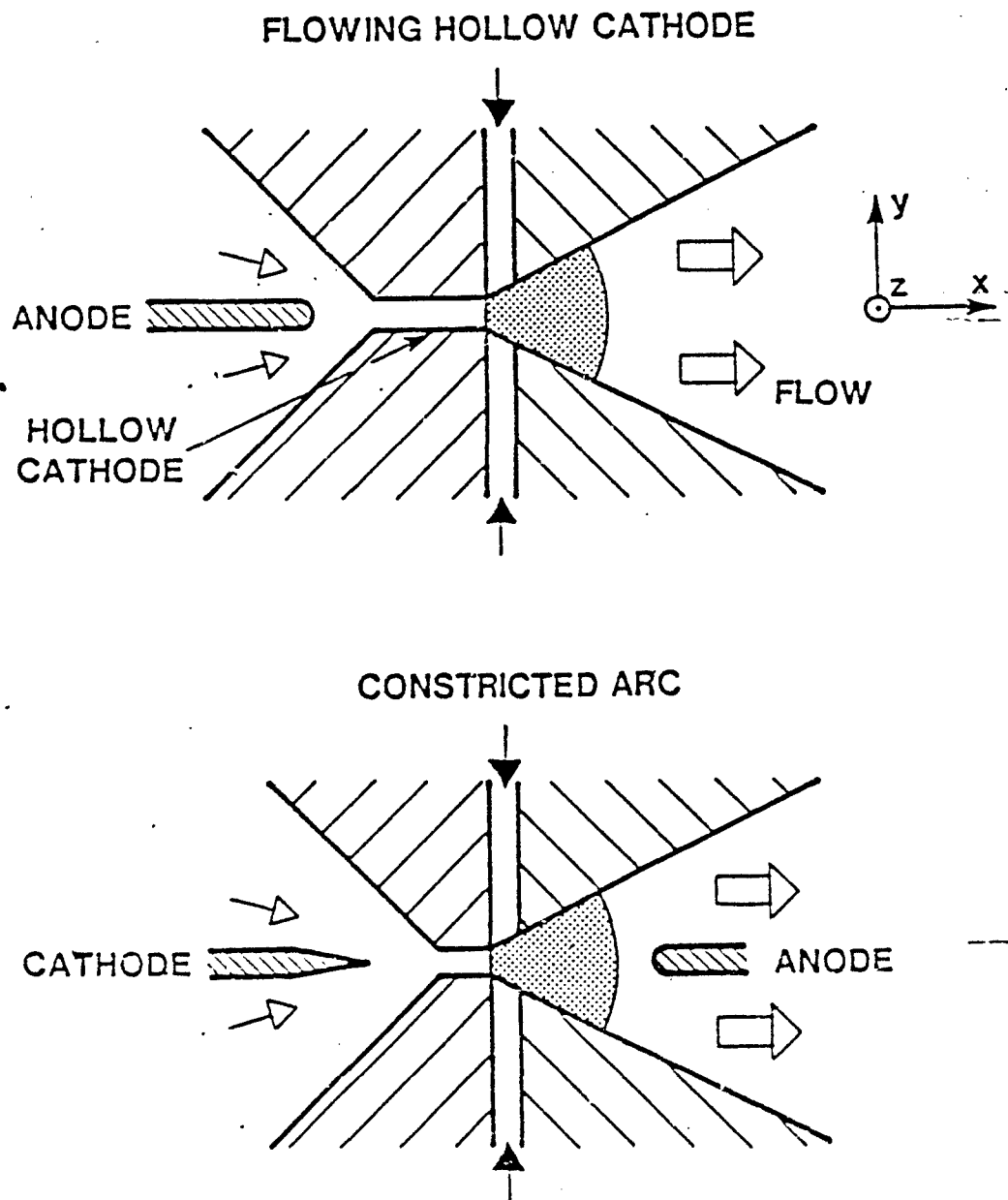


Fig. 1. Geometries of plasma mixing devices based on a flowing hollow cathode and a constricted arc.

The hollow cathode has been optimized with respect to plasma homogeneity and lifetime. Major modifications were related to electrode configuration, hollow cathode geometry and material, and nozzle shapes. A paper describing the device [2] is attached as Appendix I.

## II.2 Constricted Arc Device

The constricted arc device generates the plasma in an arc discharge which is wall stabilized and has its smallest cross section in the nozzle. The nozzle in its full length is therefore the regime with the highest plasma density and the highest electron density. The achievable plasma densities in this system are much higher (at least by a factor of  $10^2$ ), however, the combination of higher electron density and energy in the mixing zone allows significant excitation through electron collisions, making the analysis of the spectroscopic results much more difficult. The maximum metastable density should be approximately the same as in the hollow cathode [4].

A new constricted arc system has been designated, constructed, and optimized. The present system operates with a parallel plate thoriated tungsten cathode, a tungsten slit with a cross section of  $0.5\text{mm} \times 10\text{mm}$ , a tungsten nozzle, and a copper anode. It has been operated up to currents of 20A at voltages of approximately 120V.

The electron density of the flowing plasma was measured by adding  $\text{H}_2$  to the plasma gas and measuring the Stark Broadening of the Balmer lines [5]. The maximum densities achieved with He as the plasma gas with the flowing hollow cathode device was  $n_e \leq 10^{14}\text{cm}^{-3}$  and with the constricted arc devices was  $n_e \approx 10^{15}\text{cm}^{-3}$ . Increase of electron density with the discharge current was observed.

Both systems have their advantages, depending on the different types of applications, and both have been used extensively for investigations with different gas combinations. At this time, only single discharge experiments have been performed, limiting the length of the active volume to  $\leq 20\text{mm}$ . The constricted arc also tends not to fill the full slit width if operated at high pressure. Initial experiments with 3 parallel arcs showed that the active length can be increased by parallel operation of a large number of arcs.

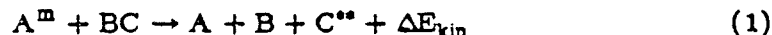
Extensive measurements have been performed on the extension of the active volume in the mixing zone by mapping the fluorescence intensity (in the x- and y-coordinates in Fig. 1) for gas combinations generating excited atoms, molecules, and excimers. An example of an emission profile is shown in Fig. 3, Appendix III. Typical cross sections are 0.5-1.0mm depending on nozzle configuration, outlet pressure, and the collision cross section for the excitation process. The smallest active volumes were achieved for excimers ( $\text{KrF}$ ).



### III. INVESTIGATION OF ENERGY AND CHARGE TRANSFER PROCESSES

#### III.1 Excited Atoms - Dissociative Excitation

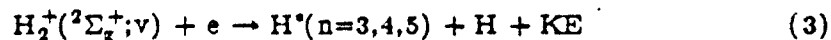
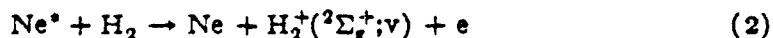
Energy transfer dissociative excitation is a mechanism involving two steps, the transfer of energy to a molecule into a repulsive branch of the potential energy and the subsequent dissociation into fragments, one of which is excited.



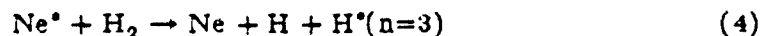
In most cases, the starting molecules are two-atomic molecules and the fragments are atoms. The energy available for excitation is the difference between the excitation energy of the metastable atom ( $A^m$ ) and the sum of the dissociation energy of the molecule  $BC$  and the kinetic energy of the dissociation products released during the dissociation process. Of special interest are therefore molecules with low dissociation energy.

This mechanism allows excitation of atomic species which under normal conditions are found as gases only in molecular form such as the halogens, oxygen, nitrogen, sulfur, carbon, etc.

**Hydrogen (H):** The emission of hydrogen Balmer series and laser oscillation of  $H_\beta$  at 486.12 nm and  $H_\gamma$  at 434.06 nm in hydrogen-near discharge has been reported by Dezenberg et al. [8]. Two step excitation of hydrogen was proposed as the main excitation mechanisms of the Balmer series and the laser oscillation.



Feld [7] proposed that direct dissociation of hydrogen by near resonant energy transfer from near metastable could be utilized to populate the upper level of Balmer  $\alpha$  line.



Upon consideration of the energy of neon metastables (16.6 and 16.7 eV) and the dissociation energy (4.47 eV) of a hydrogen molecule we have found that only the states  $n \leq 3$  can be excited by direct dissociative energy transfer process.

Experiment with the fast plasma mixing device using helium-neon mixture as the plasma and  $H_2$  as the molecular gas, showed strong fluorescence of the hydrogen Balmer  $\alpha$  line at 656.28 nm. The other lines of the series were not observed. We also did not detect emission from any other atomic or molecular hydrogen systems. If the plasma source was operated with pure helium,

emission of  $H_{\alpha}$  and other lines of the hydrogen Balmer series were not observed.

The excitation mechanism of  $H_{\alpha}$  line, in the plasma mixing device is due to the direct dissociative energy transfer from neon metastables (Eq. 4). Figure 2 shows the intensity of  $H_{\alpha}$  line vs. neon percentage in helium-neon plasma.

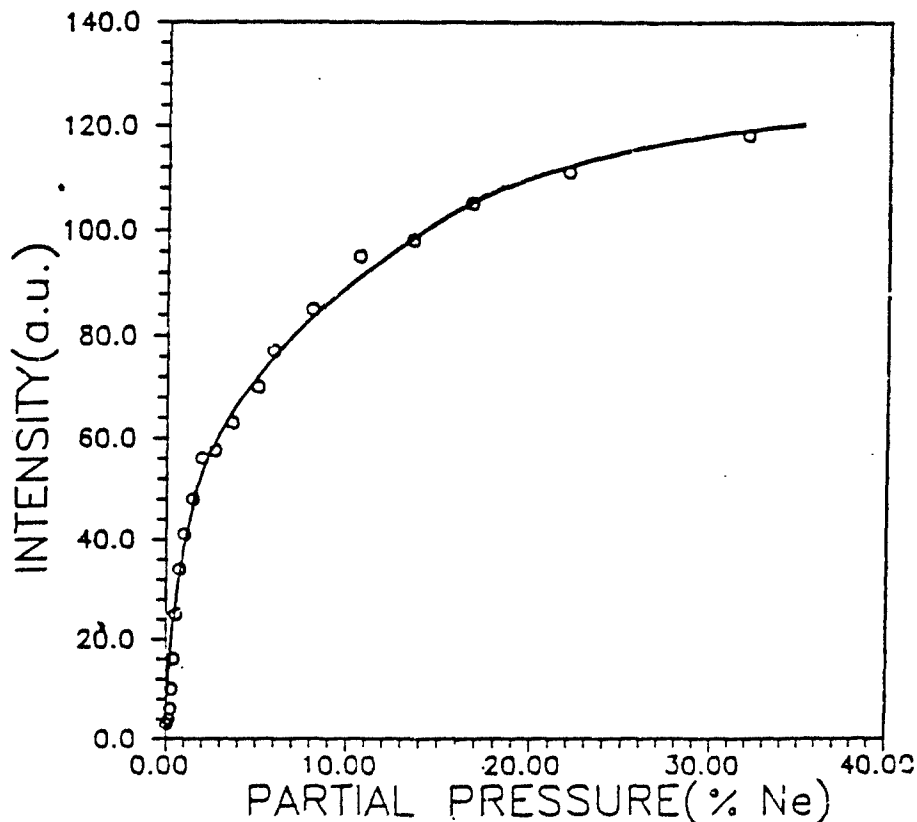


Fig. 2 Fluorescence intensity of  $H_{\alpha}$  ( $\lambda=656.3\text{nm}$ ) versus the fraction of neon to helium in the plasma source.

Contrary to the strong fluorescence at  $6562.8\text{\AA}$ , the laser oscillation at this line was not observed.  $H(n=3)$  excited state is also the upper level of Lyman  $\beta$  line at  $1025\text{\AA}$ . The Einstein coefficients of these two levels;  $3p^2P^o$  ( $L_{\beta}$  line) and  $3d^2D$  ( $H_{\alpha}$  line) are of the same order of magnitude ( $\sim 10^7\text{sec}^{-1}$ ) and the energy difference between these levels is approximately  $10^{-4}\text{eV}$ . Considering the dissociative resonant energy transfer reaction of Eq. (4), one would expect excitation of the states  $n=2$  and  $3$ , and hence a consequent emission of  $L_{\beta}$  and  $L_{\alpha}$  as well as  $H_{\alpha}$ . However, we were not able to observe any emission of

Lyman series because they lie outside the range of the equipment used in the experiment for spectroscopic investigation. As a result of this, we cannot calculate transition rates and branching ratios of the excitation and cannot give a solid explanation for not obtaining laser oscillations.

Similar experiments with the constricted arc plasma mixing device with pure helium showed fluorescence on all Balmer lines. If neon was added, the intensity of Balmer  $\alpha$  increased slightly, while the intensity of the other Balmer lines decreased.

**Carbon (C):** No fluorescence was observed on the 8335 Å transition of atomic carbon if a helium plasma was crossed with a CO beam, indicating that the energy transfer collision is not efficient.

**Oxygen (O):** Dissociative energy transfer collisions to  $O_2$  were utilized to achieve CW laser operation at 8446 Å in atomic oxygen. A paper describing these experiments and discussing the excitation mechanism [8] is attached as Appendix II.

**Fluorine (F):** Dissociative energy transfer collisions to  $F_2$  were utilized to achieve CW laser operation on the lines 7037 Å, 7128 Å, and 7311 Å. The 7311 Å line was operated CW for the first time. A paper describing these experiments and discussing the excitation mechanism [9] is attached as Appendix III.

### III. 2 Excited Molecules and Molecular Ions

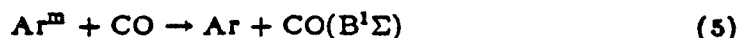
Excited molecules are candidates for CW laser operation if the lower state is depleted through fast optical decay. Such transitions can be excited through energy transfer collisions to hydrogen ( $H_2$ ), and carbon monoxide (CO). Other transitions end in metastable states such as the UV laser transition in  $N_2$ . At high pressures, it should be possible to deplete the lower laser states, either through vibrational relaxation or quenching of the electronic state. Transitions to the electronic ground state can only be depleted through vibrational relaxation. In the following, we will only present a few experiments on characteristic examples of energy transfer collisions yielding excited molecules.

Excited molecular ions have been generated through charge transfer collisions of atomic or molecular helium ions ( $He^+$ ,  $He_2^+$ ) with diatomic molecules such as  $N_2$ ,  $O_2$ , and CO.

**Hydrogen ( $H_2$ ):** Excitation into the E-state (the upper state of the IR-laser transitions) require an energy of approximately 12.5 eV. No metastables of this energy are available. Experiments with metastables of higher energy (He and Ne) showed no fluorescence on the E-B transition. The UV transitions are not accessible with our monochromator.

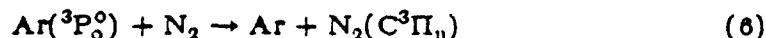
**Carbon monoxide (CO):** In experiments with argon in the plasma source and CO, we observed fluorescence on the Angstrom System (B-A) of CO.

Excitation thorough near resonant energy transfer collision



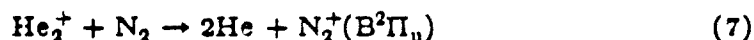
produces mainly  $v=3,4$ . The lower states (A) of the Angstrom System decay optically into the CO ground state (X).

Nitrogen ( $\text{N}_2$ ): The upper state of the UV- $\text{N}_2$ -laser can be excited through energy transfer collisions with metastable argon atoms



Experiments performed with the flowing hollow cathode plasma mixing device showed strong fluorescence on the C-B transitions if the plasma source was operated with argon or a helium-argon mixture, but not with pure helium. No other emission in the visible or near UV was observed. The evaluation of the branching ratio for the excitation process showed that more than 70% are excited into  $\text{C}(v=0)$  [10] (see Appendix IV), demonstrating the high selectivity of energy transfer collisions.

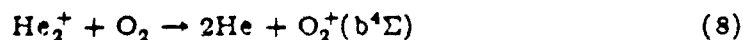
Nitrogen ( $\text{N}_2^+$ ): Charge transfer from  $\text{He}_2^+$  to  $\text{N}_2$  can be utilized to generate excited  $\text{N}_2^+$  ions for pulsed laser action on the B-X transition [11]



Experiments performed with the flowing hollow cathode device showed strong B-X fluorescence if the plasma source was operated with pure helium. This fluorescence disappeared if any other rare gas was added to the plasma flow. More than 90% of the  $\text{N}_2^+(\text{B})$  molecular ions were excited into  $v=0$ , again demonstrating the high selectivity of this charge transfer process. A paper describing the experiment and discussing the excitation mechanism [10] is attached as Appendix IV.

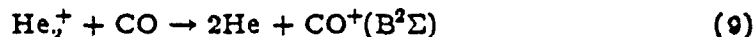
Experiments performed with the constricted arc device showed quite different results. The strongest  $\text{N}_2(\text{C-B})$  emission was still observed with argon plasmas and the strongest  $\text{N}_2^+(\text{B-x})$  emission was observed with pure helium plasmas but emission on both transitions was always present. This demonstrated the contribution of the excitation through electron collisions in the constricted arc.

Oxygen ( $\text{O}_2^+$ ): Charge transfer collisions from  $\text{He}_2^+$  to  $\text{O}_2$  were proposed as an excitation mechanism for the  $\text{O}_2^+$ -ion laser [12].



Experiments with the flowing hollow cathode plasma mixing device showed no significant fluorescence on the expected (b-a)-transition although we know from the  $\text{N}_2^+$ -measurements that a sufficient  $\text{He}_2^+$ -density reaches the mixing zone. We conclude that the process (8) is not efficient.

Carbon monoxide ( $\text{CO}^+$ ): In experiments with a helium plasma and CO we observed strong (B-A) and (B-X) emission. Only  $v=0,1$  are excited. From energy considerations we conclude that charge transfer from  $\text{He}_2^+$  dominates.



### III.3 Excimer Generation - Rare Gas Halides

Excimer generation (rare gas halides) has the advantage that both rare gas metastables and ions can be utilized in the excitation process. In a discharge consisting of rare-gas atoms and halogen molecules, the rare-gas halides are produced through two channels:

Neutral Channel:



Ionic Channel:



For high density plasma sources the ionic reaction will be dominant. Figure 3 shows a fluorescence spectrum of  $\text{KrF}$  produced with our CW flowing hollow cathode plasma mixing device at pressures of 100-300 mbar, and for comparison, the pulsed spectrum presented by Rokni, et al. [13] in the pressure range of 0.5 to 4 atm. These measurements show that the halfwidth of the  $^2\Sigma-^2\Sigma$  transition seems to be almost independent of pressure in the range from 0.1 to 4 atm although the rotational distribution at low pressure is somewhat smeared out. A clear advantage, however, is that the spectra obtained through fast plasma mixing show no emission from the  $^2\Pi-^2\Pi$  band and no  $\text{Kr}_2\text{F}$  emission, demonstrating the high excitation selectivity of this method. Equivalent measurements have been performed with  $\text{ArF}$ . At this time, we do not have a purgeable monochromator; therefore, only the product of  $\text{ArF}^*$  emission and  $\text{O}_2$  absorption could be observed.

Figure 4 shows a fluorescence spectrum of  $\text{XeCl}$  produced with a CW-fast plasma mixing device and the spectrum obtained in a mixture of Xe and Cl in argon and presented by Brau et al. [14]. We were only able to obtain emission of  $\text{XeCl}$  excimer generation when the xenon was added into helium plasma and  $(\text{Cl}+\text{He})$  is the molecular beam. In light of the experimental findings, it is concluded that Xe metastables and ions must be produced as the first step and then collisions between energy carriers and molecules take place, and consequent excimer generation is observed in the mixing volume.

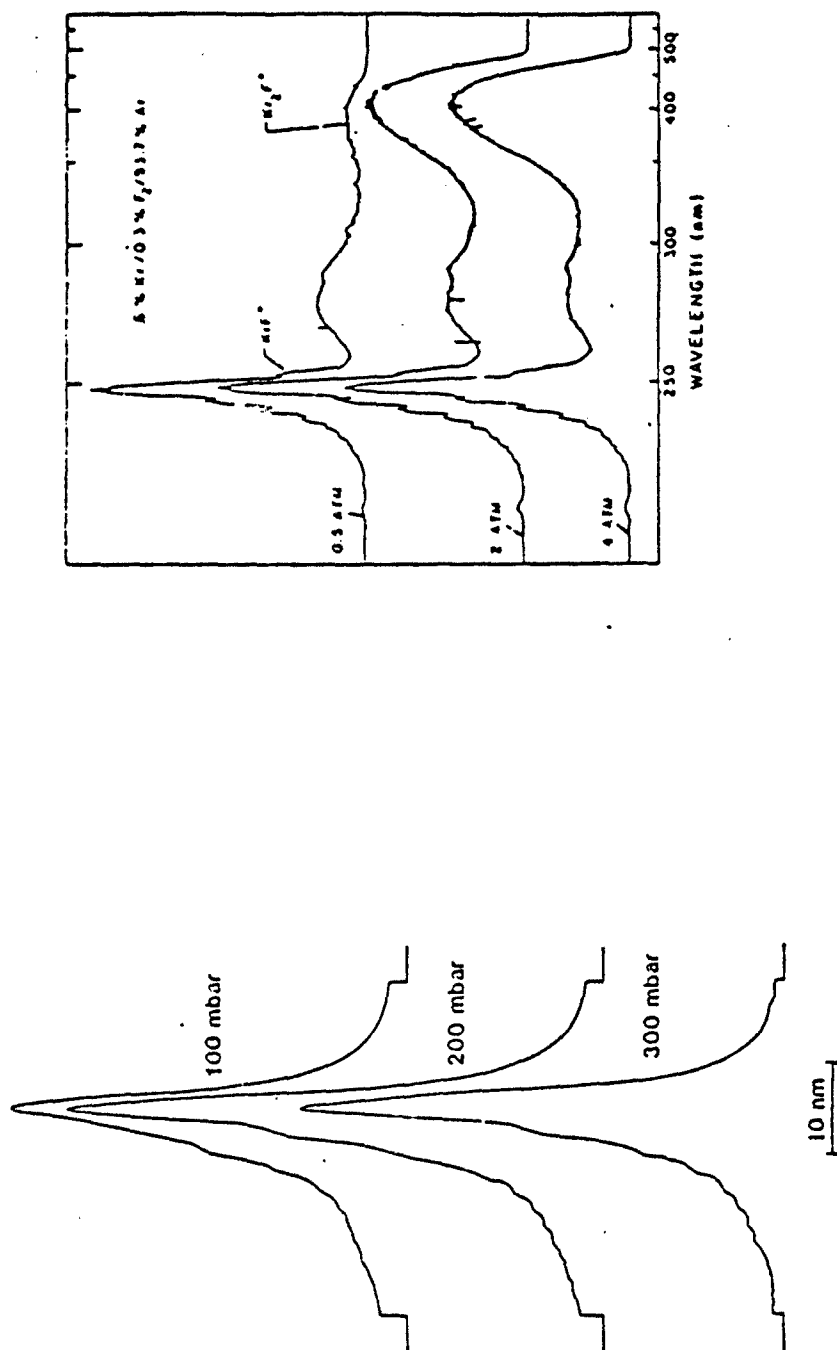
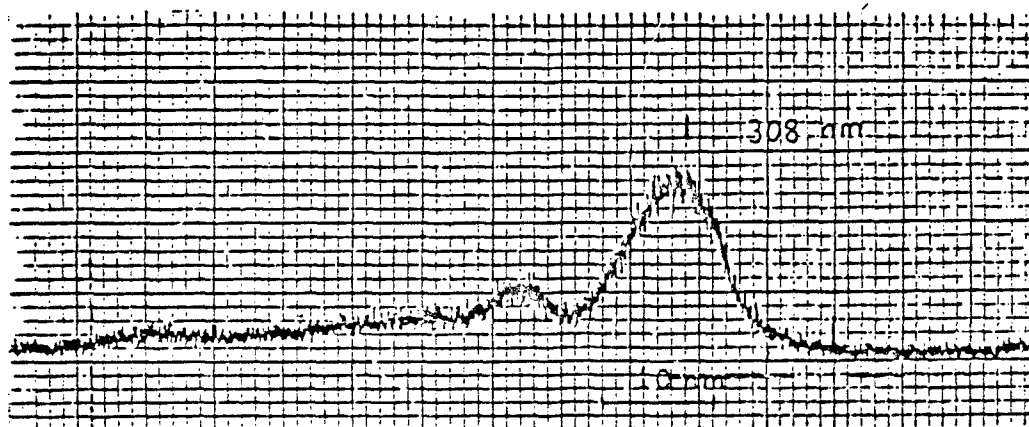
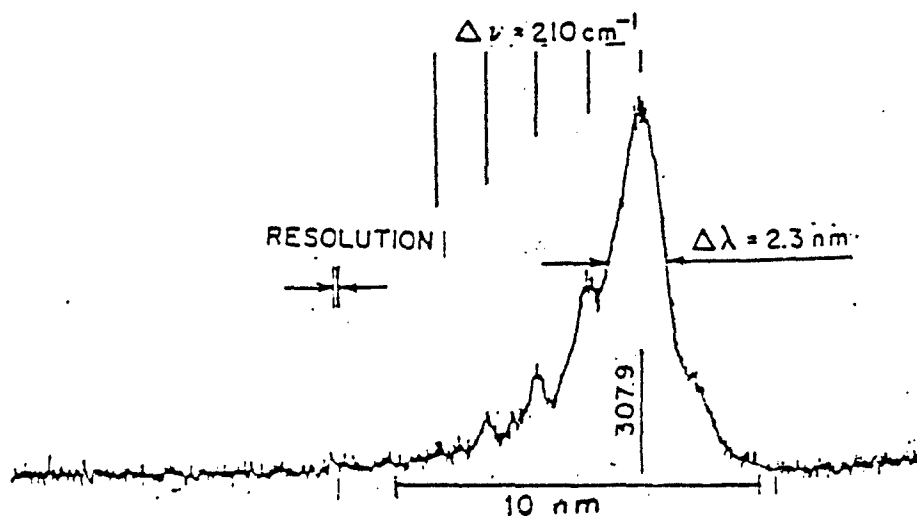


Fig. 3 Spectra of KrF excimer fluorescence at various pressures  
 Left: CW plasma mixing  
 Right: Pulsed discharge (Rokni et al., 1978)



(a)



(b)

Fig. 4 Emission spectra of XeCl ( $^2\Sigma \rightarrow ^2\Sigma$ ) excimer generation: (a) CW-plasma mixing (plasma beam 0.1% Xe He, molecular beam: 94% He, 5% Xe, 1%  $\text{Cl}_2$ ); (b) electron beam excitation of 10% Xe and 0.08%  $\text{Cl}_2$  in argon at a total pressure of 5 psig (C.A. Breau et al.).

#### IV. CONCLUSION

Resonant and near resonant energy and charge transfer collisions to molecules are effective mechanisms to generate population inversions in gas lasers. A new technique (fast plasma mixing) has been developed in which metastables and ions are generated separately in a flowing plasma source and then mixed with a molecular beam. Two CW systems, based on a flowing hollow cathode and a constricted arc has been designed. Experiments with several molecular systems have demonstrated selective excitation of atoms, molecules, molecular ions, and excimers. Dissociative excitation allows generating excited atoms of elements which naturally exist only as molecules. CW laser action was achieved in oxygen and fluorine and experiments were performed to clarify the excitation mechanisms. Energy and charge transfer to molecules allows generating excited molecules and molecular ions. Spectroscopic investigations allowed determining branching ratios and the geometric distribution of the excitation in the mixing volume. The branching ratio measurements confirmed the selectivity of the energy transfer mechanisms. Only one or two vibrational states of one electronic state are usually excited at significant rates. The mapping of the excitation rate in the mixing volume confirmed that fast transfer in a small volume is possible. The combination with a fast flow also allows removing reaction products from the active volume.

Fast plasma mixing devices have also been used for CW generation of rare gas halide excimers. First experiments on ArF, KrF and XeCl excimer generation were performed and the fluorescence profiles were investigated depending on operating parameters.

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# Fast Plasma Mixing—A New Excitation Method for CW Gas Lasers

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**Abstract**—"Fast plasma mixing" is proposed as a method to generate population inversions on electronic transitions for continuous lasers. Selective excitation is accomplished by preparing collision partners for excitation in two or more separate beams. Excitation in a well-defined reaction volume and a fast flow in combination with a suitable resonator will allow the fast removal of decay products from the active volume. This pumping method will allow the operation of new CW laser systems not possible with conventional discharges and CW operation of laser systems, which at this time can only be operated as pulsed lasers. A test device has been used to study the proposed excitation method. CW operation as a fluorine laser has demonstrated the general feasibility of this method. Of special interest are molecular lasers pumped by charge or energy transfer from atomic species or by chemical reactions and excimer lasers. These lasers may offer the capability of operating CW tunable gas lasers in the visible and ultraviolet spectral regime.

## I. INTRODUCTION

THE METHOD of "fast plasma mixing" is proposed to overcome two general limitations present in gas discharges for the operation of efficient CW-lasers on electronic transitions as follows:

1) In a gas discharge, there are always a large number of competing processes, and only one or a few are utilized for the excitation of the intended upper laser level. This is true also for laser systems in gas mixtures using energy transfer or charge transfer processes. For example, in metal ion lasers pumped through charge transfer from rare gas ions to metal atoms, nearly every ionization process of a metal atom through electron collision adds losses or even increases the population density of the lower laser state. There are also numerous possible excitation transfer or charge transfer processes from rare gases to molecules which now make inefficient lasers ( $\text{He}_2^+ + \text{N}_2 \rightarrow \text{N}_2^+ + 2\text{He}$ ) [1], or which have been proposed as laser candidates ( $\text{He}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + 2\text{He}$ ) [2]. Energy transfer from atomic metastables or ions to molecules cannot be used efficiently, especially in continuous gas discharges with mixtures of rare gases and molecular gases, since a significant fraction of the energy transferred through electron collisions will always go into excitation and ionization of the molecular gas. This has two disadvantages. First, the

energy transferred to the molecules through electron collisions is lost, and second, the molecules are now distributed over a large number of excited states. Resonant energy transfer will then only occur with molecules in some of these states, and it will also generate excited molecules in different states.

2) A large number of laser systems are self-terminating. The reasons can be that the lifetime of the lower laser level is too long, that the starting species for excitation are depleted, or that absorbing species are produced as a result of the excitation mechanism. Typical examples of the latter two problems are offered by excimer lasers.

Fast plasma mixing is, therefore, proposed as an excitation method for gas lasers which will combine the two following major advantages.

1) Excitation of states with high selectivity not possible through other mechanisms; consequently, operation of new laser systems can be achieved. Of special interest are systems based on energy or charge transfer processes from atomic species to molecules. Such processes can produce excited molecules and excimers, and subsequently, they will open the possibility of operating tunable lasers. Fast plasma mixing can also be used for laser systems based on fast chemical reactions. Here, one or two beams can be used to create suitable radicals.

2) Continuous wave laser action can be achieved in systems which otherwise are terminated after some time by bottleneck or quenching processes.

Plasma mixing has been utilized in the past for creating population inversion between vibrational states in molecular gases. The lifetimes of the electronic transition considered here, however, are shorter by orders of magnitude. These shorter time constants impose significant constraints on the mixing process and the requirements for the removal of the reaction products from the laser volume.

## II. PRINCIPLE OF FAST PLASMA MIXING

A general scheme of an excitation method using "fast plasma mixing" is shown in Fig. 1. Two different particle beams (beam 1 in x-direction and beam 2 in y-direction) are crossed within the laser volume. In general, a mixing with more than two beams in several steps is possible.

The laser resonator would be oriented in the z-direction. To generate an excitation volume with gain over a sufficient length, the cross sections of the two beams can

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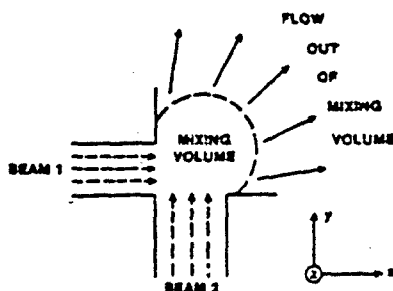


Fig. 1. Schematic sketch of fast plasma mixing.

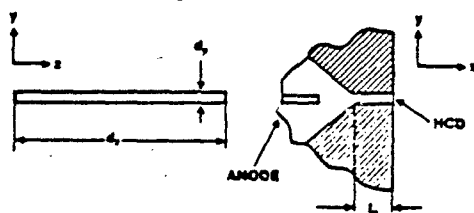


Fig. 2. Slit hollow cathode for fast flow.

be rectangular, as produced by slit nozzles extended in the  $z$ -direction (see Fig. 2), or an array of nozzles lined up in the  $z$ -direction can be used.

At least one of the two beams has to carry excited species at high densities (preferably long living species such as metastables, radicals, and/or ions). These species can be produced in different ways, such as with an electron beam, with a dc or microwave plasma torch, with a fast-flowing hollow cathode discharge, with a hollow cathode arc, or with a laser plasmatron. The species excited into the intended level are then produced through collisions of particles from different beams. It should be mentioned that a focused electron beam, crossed with a particle beam, can also generate a plasma condition as proposed here.

Let us assume that the cross sectional area of beam 2 and its flow rate are smaller than beam 1, although its velocity may be higher. The mixing depth for fast mixing will then be the penetration depth of the particles of beam 2 into beam 1. Assuming a gas-kinetic cross section in the order of  $4 \times 10^{-15} \text{ cm}^2$  and a pressure of 10 mbar, the mean free path will be in the order of  $10 \text{ } \mu\text{m}$ . Fast mixing will then occur within a few mean free paths. If the atomic weight of the particles in beam two is significantly higher, a full momentum transfer will require a larger number of collisions, increasing the diameter of the mixing volume. Mixing volumes for fast mixing with diameters of some  $100 \text{ } \mu\text{m}$  at 10–100 mbar seem to be possible.

The transit time of the particles through the active medium will depend on the beam waist diameter of the laser resonator and on the particle velocity. Assuming a circular cross section of the active volume with a diameter of  $0.1 \text{ mm}$  and a particle velocity of  $v = 500 \text{ ms}^{-1}$ , the total time for a particle to cross the active medium within the resonator will be  $t = 20 \text{ ns}$ . Such a device will fulfill the following advantages:

- 1) Selective excitation of specific states with high pump

rates is possible, since the reaction partners which will create the final species can be produced independently (in separate beams) without interference, and the production of these reaction partners can be accomplished over a long path length (long time period, respectively) until mixing occurs. The preparation of the particles of two beams can use different methods depending on the requirements for optimum production of these species. In one beam, a molecular gas may even be cooled to assure a high population density of the ground state.

- 2) The volume for excitation of the final states with high pump rate is the well-defined volume in which mixing of the two beams occurs. The fast flow of the particles will remove the reaction products fast from the volume where excitation occurs, and subsequently, accumulation of decay products in the active volume is avoided.

It should be mentioned here that large mixing volume cross sections can be produced if the excited species are produced in beams at lower pressures with higher particle velocities, such as in a hollow cathode arc. Mixing in a volume with a much larger cross section can also be allowed for laser systems which are not self-terminating or for which the time constant for self-termination is long.

### III. FAST FLOWING HOLLOW CATHODE DISCHARGES

As mentioned before, there are several methods possible for performing the initial excitation of particles in one of the particle beams, such as electron beams, arc discharges, hollow cathode discharges (HCD), lasers, and others. For a first approach, the HCD seems to combine some advantages as follows:

- 1) A hollow cathode is a fairly simple device, for example, compared to an electron beam.

- 2) The plasma in the afterglow of a fast flowing HCD can be considered as a cold plasma. This means here that the fast electrons responsible for the electronic excitation and ionization of the gas in the HCD only exist in the active region of the cathode and not in the flowing afterglow where plasma mixing will occur. This feature will allow limiting the number of excitation processes in the mixing regime to those processes intended. Such processes will mainly be near resonant processes such as excitation transfer and charge transfer collisions, attachment, and/or chemical reactions.

Hollow cathode discharges (HCD) which fulfill all requirements for fast plasma mixing have not yet been investigated. These requirements are:

- 1)  $p \times d = 10\text{--}100 \text{ mbar} \times \text{mm}$  (condition for HCD operation),  $p$ : pressure at the exit of the HCD, and  $d$ : HCD width in the direction of the crossing beam.

- 2)  $v_{\text{out}} > 100 \text{ ms}^{-1}$ ,  $v_{\text{out}}$ : flow velocity at the exit of the HCD.

- 3) Mixing region extended in the direction perpendicular to the two crossing beams.

- 4) High power density in the HCD discharge.

A preliminary test device using a slit-type hollow cathode with the following dimensions was constructed (see Fig. 2).

HCD cross sections  $d_y = 80 \mu\text{m}$ ,  $d_z = 20 \text{ mm}$

HCD length:  $l_x = 0.8 \text{ mm}$

Cathode material: copper

Anode: array of tungsten pins.

This device was tested with helium in the following operation parameter range:

Inlet pressure of HCD:  $p_{\text{in}} = 100\text{--}1200 \text{ mbar}$

Outlet pressure of HCD:  $p_{\text{out}} = 1\text{--}200 \text{ mbar}$

Current:  $I = 0.02\text{--}2.0 \text{ A}$

Voltage:  $V = 220\text{--}230 \text{ V}$ .

#### IV. FIRST TEST OF FAST PLASMA MIXING AS A PUMP SOURCE FOR A LASER

##### A. Plasma Mixing Chambers

A plasma mixing device was constructed and operated as a He-Ne laser and as an F laser (He-F<sub>2</sub>) to test the general feasibility of "fast plasma mixing" as an excitation mechanism for lasers. The plasma source (beam 1) was a fast flowing hollow cathode operated in a slit nozzle with a cross section area of  $80 \mu\text{m} \times 20 \text{ mm}$  as described in Section III. The crossed beam (beam 2) was generated by a second slit nozzle with a cross sectional area of  $25 \mu\text{m} \times 20 \text{ mm}$ , which was positioned directly at the exit of the hollow cathode under an angle of  $90^\circ$  (see Fig. 1). The hollow cathode was operated with helium and the gases used for the crossed beam were neon, or F<sub>2</sub>, respectively. The flow rates through the nozzle were controlled by adjusting the inlet pressures. The pressure in the mixing chamber was controlled with a valve, varying the pump speed of a high capacity rotary pump.

##### B. Resonator

The resonator was oriented in the z-direction, perpendicular to both beams (see Fig. 1). Internal mirrors were used which were protected against contaminations from the mixing chamber by a slight flow of helium.

The proposed excitation mechanism itself will impose certain constraints on the resonator used, since the cross section of the pump volume will be limited. The major restrictions, however, will come from the specific laser system. If long-living species are excited, or if the laser system is continuous in nature, then the active volume may be quite large and the resonator will only have to be optimized with respect to the efficient use of the active volume. If, however, a laser system is used which otherwise can only be operated in a pulsed mode, then the cross section of the active medium will be limited to the distance, the excited beam particles travel within the time which corresponds to the maximum pulse length in the pulsed system.

As an example, one may consider a plasma mixer for a laser excitation mechanism which otherwise would only allow pulsed operation up to pulse lengths of 100 ns. Even

TABLE I  
THRESHOLD CONDITIONS FOR CW LASER ACTION

	He-Ne laser	F laser
Inlet pressure of HCD: $p_{\text{in}}$	250 mbar	350 mbar
Outlet pressure of HCD: $p_{\text{out}}$	13.5 mbar	30 mbar
Hollow cathode current: $I$	0.02 A	0.05 A
Hollow cathode voltage: $V$	223 V	220 V
(He-Ne; He-F <sub>2</sub> )-flow ratio	3:1	5:1

with a flow velocity of  $10^3 \text{ ms}^{-1}$ , one would get a cross section of the active medium of  $100 \mu\text{m}$ . This restriction requires the use of a resonator with a small beam waist, such as a near concentric resonator.

For our first experiments to test "fast plasma mixing" as an excitation method for continuous gas lasers, we, therefore, used a symmetric, near concentric resonator. The beam waist diameter in this resonator was calculated to be  $85 \mu\text{m}$ . The dependence of the beam diameter on the distance from the beam waist can be neglected since the active medium is only 2 cm long.

After proper alignment of the fluorine laser, for example, no realignment was necessary over a wide range of operation parameters such as the pressure  $p_{\text{out}}$  in the mixing volume (at  $I = 0.8 \text{ A}$ :  $2 \text{ mbar} \leq p_{\text{out}} \leq 280 \text{ mbar}$ ) and the hollow cathode current  $I$  (at  $p_{\text{out}} = 30 \text{ mbar}$ :  $0.05 \text{ A} \leq I \leq 2.0 \text{ A}$ ). We therefore conclude that optical distortion due to gas dynamic motion was not severe.

##### C. Threshold Conditions

We used a pair of highly-reflecting mirrors with a transmission  $T \leq 0.5$  percent in the wavelength range from 560 to 710 nm. The threshold conditions for CW laser operation (minimum current) for the He-Ne laser and the F laser are presented in Table I.

The power dissipated at threshold is only a small fraction of the power dissipated at the stability limit of this device at otherwise same conditions (1 percent for He-Ne, 2.5 percent for He-F<sub>2</sub>). We also have some evidence that the stability limit of the used hollow cathode can be shifted to much higher current densities through some design modifications.

##### D. New CW Laser Line in Fluorine

The fluorine laser (He-F<sub>2</sub>) in the visible- and near-IR spectral region had initially been operated in pulsed helium discharges with small admixtures of F<sub>2</sub> on a large number of identified laser transitions [3]. The dominant excitation mechanism is believed to be energy transfers from helium metastables to fluorine molecules and consequent dissociation [4].

To our knowledge the fluorine laser, to date, has been operated *continuously* only using an electron beam pumped helium plasma with less than 1 percent F<sub>2</sub> or AgF as a fluorine donor on the transitions 703.75, 712.79, 720.24, and 780.02 nm [5]. With the device described above, we achieved CW laser action on the lines 703.75, 712.79, and 731.10 nm. The line 780.02 nm was not in

the wavelength range in which our resonator had sufficient low losses. We are not able to give any reasons to why the line 720.24 nm was not observed in our experiment or why the line 731.10 nm was not observed in experiments using the electron beam as a pump source. The same discrepancy is found in papers on pulsed discharges operated at low pressures ( $< \text{mbar}$ ) [3], [4].

The line 731.10 nm was operated *continuously* for the first time. From the transmission losses of the resonator mirrors at this wavelength we conclude that the gain was at least  $0.75 \text{ percent} \cdot \text{cm}^{-1}$ .

#### V. SUMMARY

"Fast plasma mixing" is proposed as a new method for generating population inversions on electronic transitions continuously. The excitation processes mainly considered are near resonant charge or energy transfer processes. Selective excitation is accomplished by preparing the collision partners for excitation in separate beams. Excitation in a defined volume and a fast flow allows the fast removal of excitation products from the active laser volume. Fast flowing hollow cathode discharges operated in slit nozzles are considered as excitation sources for the particle beams.

A test device, with a slit hollow cathode discharge in helium, crossed with a beam of  $\text{F}_2$ , was operated as a CW atomic fluorine laser. One fluorine laser line has been operated *continuously* for the first time. The gain of this line was  $0.75 \text{ percent} \cdot \text{cm}^{-1}$ .

It is expected that gas lasers on electronic transitions in molecules can also be operated continuously using "fast plasma mixing" as an excitation method.

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## APPENDIX II

### ON THE EXCITATION MECHANISM OF THE OXYGEN LASER IN A FAST PLASMA MIXING DEVICE

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#### Abstract

A flowing hollow cathode rare gas plasma crossed with an oxygen ( $O_2$ ) beam was used to operate the atomic oxygen laser at  $8446.7 \text{ \AA}$ . Laser action based on energy transfer collisions was accomplished only with pure helium plasmas. With additions of 0.2% neon or 0.1% argon to the helium plasma, the laser ceased to operate and fluorescence was reduced. No fluorescence was observed if other O-donors such as CO,  $CO_2$  or  $N_2O$  were used. The excitation mechanisms for different O-donor and rare gas combinations and different excitation methods are discussed.

## Introduction

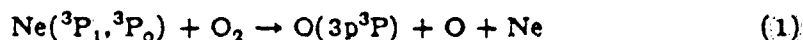
In recent papers [1,2] we discussed the possibility of using crossed beam devices to utilize near resonant energy transfer collision between metastable atoms and ground state molecules to generate population inversions. The combination of energy transfer collisions with dissociative excitation can provide an efficient pump mechanism for gas lasers. This concept, in combination with a crossed beam device, was first realized with a helium plasma beam crossed with a beam of a mixture of helium and  $F_2$  to operate the atomic fluorine laser [2]. In this paper we present similar experiments with one rare gas plasma beam and one beam containing oxygen ( $O_2$ ) for the operation of the atomic oxygen lasers. Also, results using other oxygen donors such as CO,  $CO_2$  and  $N_2O$  are presented.

The experimental setup has been described previously [1]. The two beams are generated by two slit nozzles, each with a cross section of typically  $0.1\text{mm} \times 20\text{mm}$  (Fig. 1). One beam is the flowing afterglow of a hollow cathode discharge operated with helium and additives such as neon or argon. The other beam is pure oxygen ( $O_2$ ) or one of the other oxygen donors. Since the two slit nozzles of the device are not supersonic nozzles, the speed of the species in the flow direction was estimated as  $500\text{ms}^{-1}$ . From mapping of the fluorescence profile of different oxygen lines in the xy direction and the direction perpendicular to this direction (Fig. 1), we concluded that the active volume of the intersection of the two beams was a column of approximately  $0.5\text{mm}$  in diameter and  $20\text{mm}$  in length (in z-direction, see Fig. 1). Similar fluorescence profile of one fluorine laser line was presented in a previous paper [2]. Under these conditions the transient time of the collision products in the mixing volume was approximately in the order of one microsecond. A near concentric resonator with a beam waist of approximately  $100\mu\text{m}$  was aligned

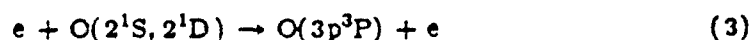
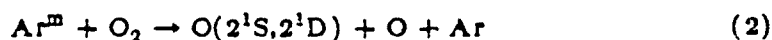
along the z-axis of this active volume. The fluorescence intensity and the laser power were measured as functions of different operating parameters such as outlet pressure, hollow cathode current, and a fraction of admixtures of neon or argon to the helium plasma. For the fluorescence measurements, the end mirrors were taken out of the cavity. The maximum power of the laser we had observed was approximately up to 1 milliwatt.

### Excitation Mechanisms of the Oxygen Laser

The atomic oxygen laser was first operated by Bennett et. al., [3] with RF-discharges in Ne-O<sub>2</sub> and Ar-O<sub>2</sub> mixtures. The atomic oxygen laser operates on the  $3p^3P_{0,1,2} - 3s^3S_1^o$  transitions (see Fig. 2). The lifetimes of the upper states are  $\sim 36$  ns while the lower state decays into the ground state in 2.6 ns [14], which makes this system suitable for continuous laser operation. Accumulation of atomic oxygen and large discharge volumes favors resonance radiation trapping, which can prevent CW population inversion. The dominant excitation mechanism proposed for the Ne-O<sub>2</sub> mixture was a near resonant energy transfer from Ne-metastables to O<sub>2</sub> and subsequent dissociation (dissociative excitation):



The excitation mechanism proposed for the Ar-O<sub>2</sub> mixture was a dissociative excitation energy transfer into lower lying singlet states and a subsequent excitation through electron collisions:



The fact that only the  $^3P_2 - ^3S_1^o$  transition showed laser oscillation and the  $^3P_1 - ^3S_1^o$  transition did not, was explained by an overlapping absorption line of



ozone [4]. When the laser tube was cooled with liquid  $N_2$ , all three  $^3P_{0,1,2} - ^3S_1^0$  transitions showed laser oscillation [5].

The addition of large amounts of helium to Ne- $O_2$  discharges improved laser operation significantly [6]. As a possible explanation, it was suggested that the neon metastable density can be increased through energy transfer from helium metastables to neon and consequently decay into the metastable state of neon. Experiments with He- $O_2$  mixtures have not been reported previously.

In several experiments, laser action was only observed on the wings of the spontaneous emission profile [7-10]. This behavior can result from a broader velocity distribution of atoms in the upper laser state than in the lower state. Such conditions are possible if the upper state is excited through dissociative excitation (reaction 1 or 2) [11] and the lower state population is maintained at a similar high value as a consequence of resonance radiation trapping, especially in a cooled laser tube [9,10]. Therefore, the velocity profile of the atoms in the upper state is broad while the velocity profile of the lower state is narrow and a population inversion can exist in the wings of the fluorescence profile even if there is no population inversion of the two states as a whole.

Laser action in pure oxygen on all three transitions has also been obtained in laser tubes cooled with liquid  $N_2$  [5,12]. In pulsed discharges, laser action was observed within the discharge pulse and in the afterglow. During the discharge pulse, dissociative excitation in collisions with electrons was considered to be the dominant excitation mechanism:



meanwhile dissociative recombination was considered to generate the population inversion in the afterglow [5,12a,12b]:



It should be noted that the  $\text{O}_2^+$ -ground state is approximately 2eV below the energy of the  $\text{O}+\text{O}(3^3\text{P})$  state. A long living  $\text{O}_2^+$ -state with small energy defect is the  $a^4\Pi_u$ -state [12]. In gas discharges, especially at high values of  $E/N$ , this state is populated either directly through ionizing electron collisions or radiative via the  $b^4\Sigma_g^-$ -state. The recombination rate in the afterglow increases due to a decrease of the mean electron energy.

The oxygen laser has also been operated in helium and neon discharges with other oxygen donors such as  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{NO}$  and  $\text{N}_2\text{O}$  [4]. In all cases, a two step process was proposed similar to the  $\text{Ar}-\text{O}_2$  system (reactions 2 and 3).

#### Excitation in a Plasma Mixing Device

The operation conditions in our plasma mixing device are significantly different than in any type of gas discharge [1]. Plasma generation and mixing the afterglow plasma with the oxygen containing gas are separated. The metastables and the ions are the main energy carrier species at the exit of the slit hollow cathode where the mixing takes place. The electrons have to travel approximately two millimeter in the slit hollow cathode toward the exit, thus there is enough time for the relaxation of the electron energy distribution. Consequently, it is expected that the majority of the electrons that reach the mixing zone are low energy electrons, and they do not play a significant role in the excitation of molecular gas injected in the afterglow plasma. Therefore, it is much easier to evaluate the importance of specific proposed mechanisms, while other mechanisms, due to electron collisions, do not contribute at all. The goal of our experiments was to evaluate the contribution of the different proposed excitation mechanism to the operation of the oxygen laser in a plasma mixing device.

CW oxygen laser action was achieved when  $O_2$  was injected into a pure He afterglow plasma. Both single-mode and multi-mode laser oscillations were observed. Experiments were performed on both the laser power and the fluorescence emitted from the mixing zone depending on system parameters such as the input pressure and gas composition of nozzle 1 (the plasma source),  $p_1$ , the input pressure of nozzle 2 (the oxygen donor),  $p_2$ , the outlet pressure in the mixing volume,  $p_{out}$ , and current,  $I$ , and voltage,  $V$ , of the hollow cathode discharge. These parameters were kept at the following optimum conditions unless indicated otherwise ( $p_1=470$  mbar He,  $p_2=330$  mbar  $O_2$ ,  $p_{out}=38$  mbar,  $I=1.05$  A,  $V=220$  V). As stated above, the main objective of the experiments was to examine the excitation mechanism of the oxygen laser in a flowing system such as ours - a fast plasma mixing device. Also, the cavity modes were not noticeably sensitive to the system parameters, they were only sensitive to the end mirror's alignments. Therefore, the cavity was set for multimode laser operation at optimum operating conditions unless indicated otherwise.

In all our experiments we observed laser action only on the  $^3P_1-^3S_1$  transition at  $8446.7 \text{ \AA}$ , although the fluorescence intensity of the  $^3P_2-^3S_1^o$  transition at  $8446.3 \text{ \AA}$  was higher. This laser line observed in our experiment was not observed in some of the early experiments since it overlaps with the absorption of one ozone line [4]. At this time, we are not able to provide any explanation especially since the individual Einstein coefficients for the three lines  $^3P_{1,2,3}-^3S_1$  are not available [14].

The dependence of the laser power on system parameters is similar to the one found for the fluorine laser [2]. Figure 3 shows the dependence of the laser power on the discharge current in the hollow cathode at otherwise optimum conditions. The saturation of the laser power with current is expected if metastable helium atoms are involved in the excitation mechanism [13]. For

comparison we also present curves of the current dependence of the fluorescence intensity of the same transition. At low currents the fluorescence intensity increases linearly with current and, at higher currents, the same saturation is observed as for the laser power. The fairly high threshold current for oxygen laser action and the fact that only the line  $8446.7 \text{ \AA}$  showed laser oscillation may come from the fact that the transmission losses of both mirrors, 1.3%, were fairly high, corresponding to a gain of 0.65%/cm at threshold. From the fluorescence intensities at threshold and at maximum laser power we estimated the maximum gain to be  $g_m = 2.25\%/cm$ . This number is conservative since only the transmission losses have been considered.

Figure 4 shows the dependence of the laser power on the pressure in the mixing volume. In the low pressure regime the power is limited since the collision frequency is too low for efficient energy transfer. This can be explained by looking at the fluorescence profile of the emission at different pressures. At low pressures the fluorescence intensity is low and a secondary intensity maximum is observed at about 2 to 3 mm away from the first intensity maximum [2]. In the high pressure regime the molecular beam does not penetrate the afterglow plasma. The fluorescence intensity starts decreasing with increasing pressure, so efficient energy transfer from the afterglow plasma to the molecular gas is not achieved.

The laser power ( $8446.7 \text{ \AA}$ ) decreased if either neon or argon was added to the helium in the hollow cathode. Figure 5 shows the dependence of the laser power on the neon- or argon-fraction in the plasma. With only 0.2% neon, or 0.1% argon, the laser ceased to operate. Figure 6 shows the dependence of the fluorescence intensity of the two lines  $8446.7 \text{ \AA}$  and  $8446.3 \text{ \AA}$  on the neon- and argon-fraction. With our monochromator, we were not able to separate the two lines  $8446.36 \text{ \AA}$  and  $8446.25 \text{ \AA}$ . The addition of neon or argon again causes a

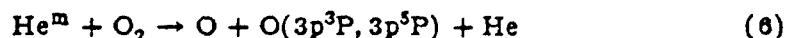
decrease in fluorescence intensities of both lines; however in the case of neon the fluorescence intensities level off to a constant value, while with argon as an additive both the fluorescence and the laser lines disappear completely. A detailed explanation to these behaviors will be given later in this section.

From these experimental results, and considering the specific operating conditions in a plasma mixing device, we can draw a number of conclusions concerning the excitation mechanism. Figure 7 shows a summary of all proposed mechanisms. In our system, oxygen containing molecules in their ground state are injected into a rare gas plasma in a small reaction volume, and all reaction products are rapidly, approximately in 1 microsecond, swept out of the reaction zone. An accumulation of oxygen atoms in the active region is, therefore, impossible and the influence of resonance radiation trapping on the population of the lower laser level can be neglected. Also, ozone generation and accumulation and absorption through ozone molecules is not possible.

In general, in a rare gas afterglow, one expects a "two-electron group" energy distribution. One group consists of thermalizing low energy electrons and the other group consists of high energy electrons generated either by superelastic collisions of electrons with metastable helium atoms, or Penning ionization in collisions between two metastable atoms. The existence of the metastable atoms and the fast electrons is visible in the afterglow of the helium plasma (or mixture of helium and other rare gas plasma) over a long distance behind the nozzle (2-3 cm in the xy-direction, see Fig. 1) as long as no molecular gas is injected into this plasma. As soon as small amounts of  $O_2$  are injected, the afterglow disappears, which indicates that the generation of fast electrons is interrupted. Therefore, it is unlikely that excitation through electron collisions from the metastable singlet states ( $^1S$  and  $^1D$ ) plays a role in our experiment. Subsequently, we exclude any reaction similar to reaction (3).

The energy stored in the flowing rare gas afterglow plasma of a hollow cathode discharge is stored mainly as excitation energy in metastables and as ionization energy. At high hollow cathode currents the metastable density saturates while the ion density increases further. The dependence of the laser power on the hollow cathode current shows the same saturation as the metastable density [4,12] even though molecular ions ( $\text{He}_2^+$ ) are the dominant ions [15] at pressures of 100 torr and above. We have to conclude that helium ions do not play a significant role in the excitation mechanism.

For pure helium discharges this leaves two channels (see Fig. 6). One is the direct excitation:



The other possibility is the generation of excited molecular oxygen ions through Penning ionization



at first; and second, the excitation of the oxygen atom through dissociative recombination according to reaction (5). In the generation of molecular oxygen ions, by collisions with helium metastables, the expected excited states are  $a^4\Pi_u$ ,  $A^2\Pi_u$  and  $b^4\Sigma_g^-$ . The state  $a^4\Pi_u$  is also populated through radiative via the  $b^4\Sigma_g^-$  state. These transitions and the transitions from  $A^2\Pi_u$  to  $X^2\Pi_g$  are allowed transitions [16] and are in the range that our spectrometer can detect. However, our spectroscopic investigation did not show any molecular emission of these transitions. Therefore, it is concluded that Penning ionization, reaction (7), is not an effective process in our device and it is unlikely that the excitation of the oxygen atom due to dissociative recombination, according to reaction (5), plays a role in our experiments. Also since in hollow cathode discharges at low currents both the metastable density and the ion density (or

electron density) increase fairly linearly with current [13] one expects a quadratic increase of the pump rate of the excited oxygen atoms with current, which is in contradiction to the linear increase of the fluorescence intensity shown in Fig. 2. We therefore conclude that for the injection of  $O_2$  into a flowing helium afterglow, only reaction (6) contributes to laser excitation.

The large energy defect between the metastable helium states and the upper laser states makes it possible for the higher lying states to be excited first and the upper laser level to be populated through optical transitions from  $ns^3S^o(n \geq 4)$  and  $nd^3D^o(n \geq 3)$ . Transitions from the  $4s^3S^o$  and  $3d^3S^o$  states are in the IR and are not accessible with our monochromator. The transition rates for the observed visible and UV-transitions, relative to the rates for the laser transitions, are given in Table I. The low radiative transition rates into  $3p^3P$  confirm that the major excitation mechanism of this state is direct dissociative excitation according to reaction (6). The  $ns^3S^o(n \geq 4)$ -states and the  $nd^3D^o$ -states also decay into the oxygen ground state  $2s^22p^4^3P$ . For most of these transitions, the Einstein coefficients are not available.

Selective excitation of the  $4p^3P_{0,1,2}$ -states should also allow CW laser action on the UV transitions  $4p^3P_{0,1,2} - 3s^3S_1^o$  at  $4368 \text{ \AA}$  since the lifetime of the upper state is  $1.5 \mu s$  and 570 times larger than the lifetime of the lower state of  $2.6 ns$  [14]. However, the much higher pump rates into the  $3p^3P_{0,1,2}$ -states which decay into the same lower state prevent a CW population inversion for this UV transition.

Besides the triplet transitions  $3p^3P - 3s^3S^o$  we also observed even stronger fluorescence on the quintet transition  $3p^5P - 3s^5S^o$  with the same current dependence as the triplet states showing that both systems are excited by the same direct dissociative excitation processes. However, the quintet transitions

did not show any laser oscillation. The lower level,  $^5S^0$ , of the transition is a long-living state with a lifetime in the order of  $10^{-3}$ s while the upper state,  $^5P$ , decays in  $3.10^{-8}$ s [14]. Therefore, the laser oscillation on this transition should not be expected.

The experiments with the addition of argon to the helium plasma confirm some of our previous conclusions. Energy transfer from metastable argon atoms to oxygen molecules only allows the generation of metastable singlet oxygen atoms (see Fig. 7). Electrons with energies larger than 5.5 eV are required for excitation of the upper laser states. The addition of very small amounts of argon ( $<0.1\%$ ) quenches the fluorescence on the laser transitions completely (Fig. 8), confirming that no high energy electrons are present in the mixing volume.

The experiments with the addition of neon to the helium plasma give quite different results. Up to an addition of  $\sim 0.3\%$  neon, the fluorescence intensity of the laser transitions ( $8446.7 \text{ \AA}$ ) decreases with neon concentration and then stays constant at approximately 43% of its maximum value (Fig. 8). The laser is well above threshold at any operating condition with a pure helium plasma yielding the same fluorescence intensity. However, with the addition of neon, the laser ceases to operate. Two conclusions can be drawn: First, the excited oxygen atoms in the upper laser state are produced through dissociative energy transfer collisions of metastable neon atoms with  $O_2$  according to reaction (1); however, this process does not seem to be as efficient as with helium metastables according to reaction (6). Second, since the laser ceases to operate, we have to assume that the addition of neon also increases the population of the lower laser level which means that reaction (1) may also have a strong channel yielding oxygen atoms in the  $3s^3S^0$  state directly. The rate for this process has to be significant since this state decays fast and resonance



absorption trapping should be of minor importance in our system.

Investigations were also performed with other oxygen donors. When CO, CO<sub>2</sub> and N<sub>2</sub>O injected into a helium plasma, no fluorescence of the 8446-7Å laser lines or any other oxygen lines were observed. In the case of CO and CO<sub>2</sub> as the oxygen donors, a two-step excitation similar to reactions 2 and 3 should be a main excitation mechanism of the oxygen laser as was proposed earlier [4]. The fact that no atomic lines were observed also confirms that energy transfer collisions with direct dissociative excitation equivalent to reaction (6) do not occur. In the case of N<sub>2</sub>O, the energy of the neon metastables is well above the total energy of binding and excitation energy of the oxygen atom, therefore, the energy requirements for a direct dissociative excitation of oxygen should be sufficient. However, no fluorescence of any atomic oxygen line was observed when N<sub>2</sub>O was injected into a neon afterglow plasma. The only observed transition was a molecular emission band in the UV (between 3400 Å and 4050 Å) which we were not able to identify, nor find any information in the literature. We know that all the excitations should be the result of near resonant energy or charge transfer collisions, because there are no high energy electrons that can play any significant role in the excitation processes taking place in the mixing volume. Therefore, this emission band should be due to a near resonant type collision. Since detailed information on the potential energy curves of N<sub>2</sub>O is presently unavailable, we are not able to tell if there is any spin conservation constraints or if the Franck-Condon principle is satisfied during the collisions for direct dissociative excitation of oxygen.

In conclusion, the excitation mechanism of the atomic oxygen laser in a plasma mixing device is quite different from the one in any kind of gas discharge device. The lack of sufficient high electron densities with sufficient

high energies, prevents the involvement of electron collision excitation in the excitation mechanism. Excitation of the molecules is then accomplished by energy transfer collisions with metastables. These energy transfer collisions provide selective excitation of a small number of states. The combination of fast flow, which provides the replenishment of the starting compounds for these collisions, and a small excitation volume, which prevents the accumulation of reaction products which may reduce the gain, favor in the excitation of one or several states. Under these conditions and the results of experimental investigations, the main excitation mechanism of oxygen laser is due to the direct dissociative excitation collisions of  $O_2$  with helium metastables (reaction (6)). Even though neon metastables generate excited oxygen atoms at the upper laser level, it seems this process is not efficient to obtain laser oscillation.

#### Acknowledgement

This work was supported by ARO. H. Kirkici was also supported by the AAUW Educational Foundation and by a scholarship from the Republic of Turkey. We would also like to thank D. Bruno and J. Preiss for their help. Special thanks goes to J. Boscher for many helpful discussions on the excitation mechanism of the oxygen laser.

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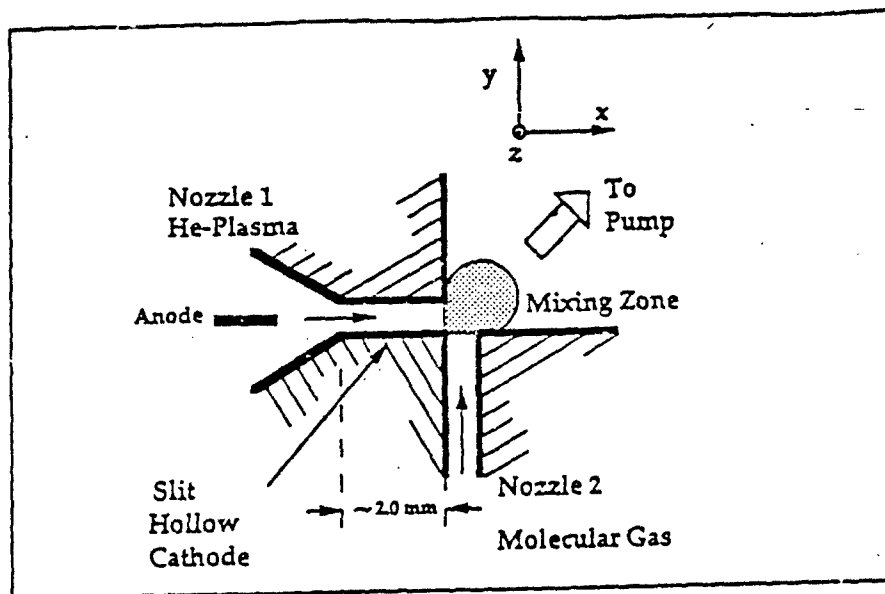
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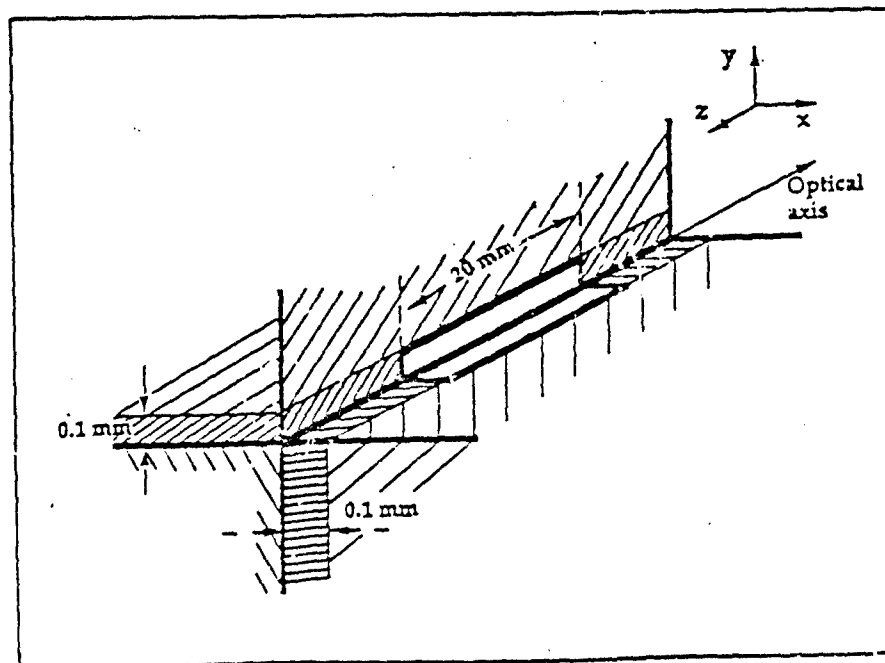
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Upper State	Lower State	Wavelength in Å	Relative Transition Rate
$3p^3P$	$3s^3S^o$	8446	100%
$4p^3P$	$3s^3S^o$	4368	2.2
$5p^3P$	$3s^3S^o$	3892	< 0.1
$4s^3S^o$	$3p^3P$	13164-5	NM
$5s^3S^o$	$3p^3P$	7254-5	0.7
$6s^3S^o$	$3p^3P$	6046	0.5
$7s^3S^o$	$3p^3P$	5555	< 0.1
$3d^3D^o$	$3p^3P$	11286-7	NM
$4d^3D^o$	$3p^3P$	7002	2.2
$5d^3D^o$	$3p^3P$	5958	< 0.1

NM: not measured



(a)



(b)

Fig. 1 Geometry of a 2-beam plasma mixing device. (a) Two-dimensional view of the electrodes and slits; (b) three-dimensional view of the slits.

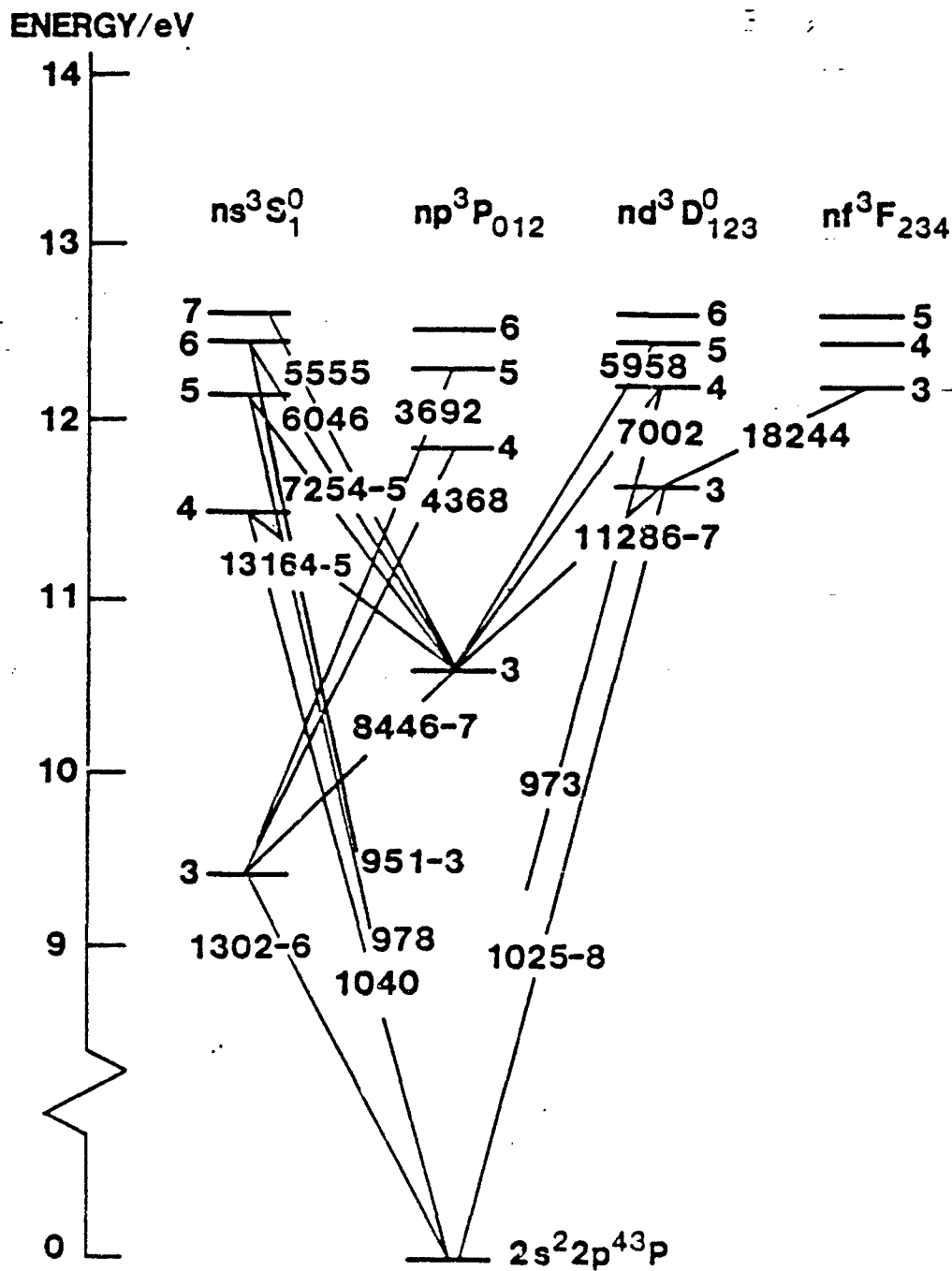


Fig. 2 OI Triplet Grotian diagram.

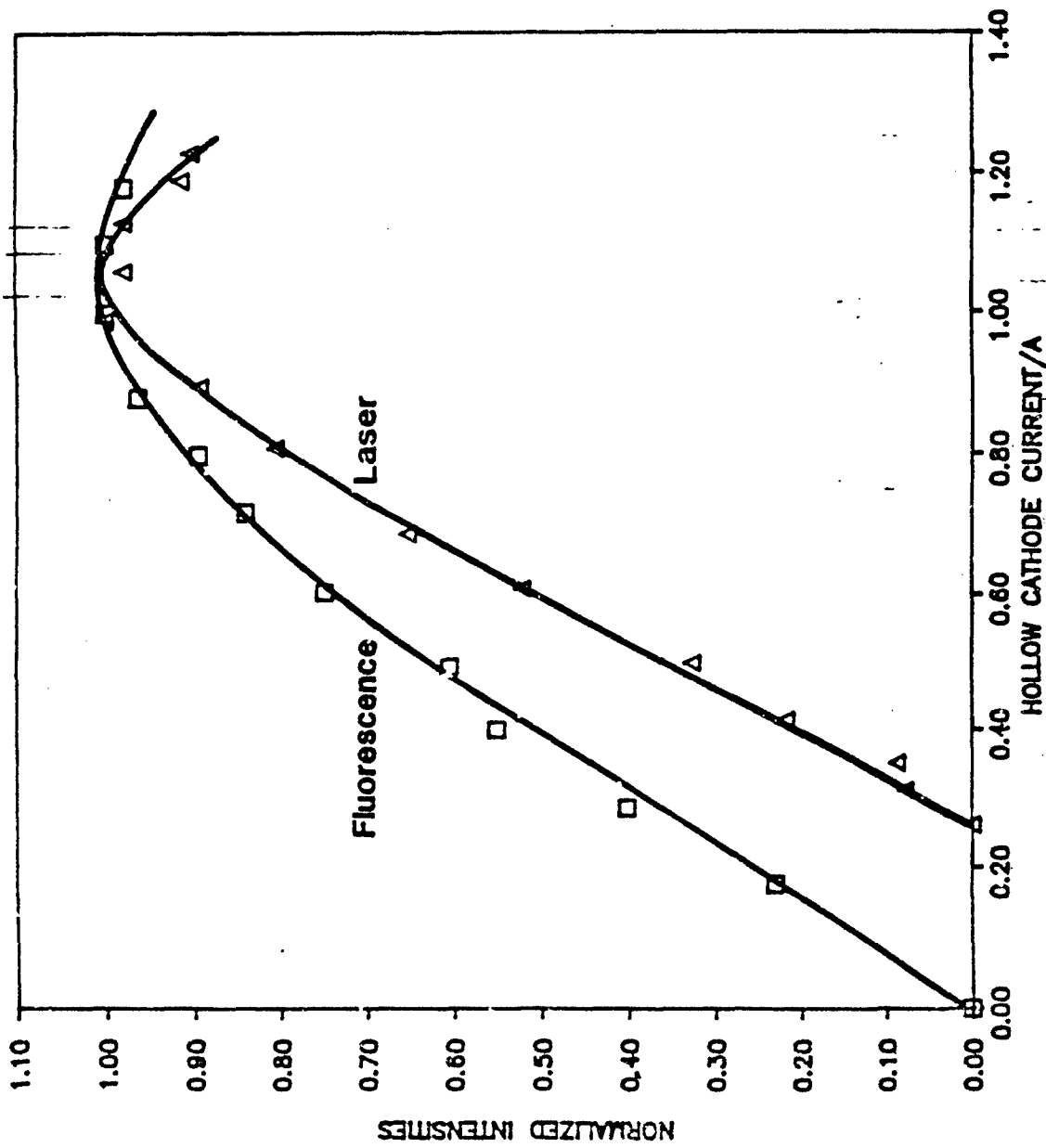


Fig. 3 Normalized laser power and fluorescence intensity (8446.7 Å) versus hollow cathode current at otherwise optimum conditions.



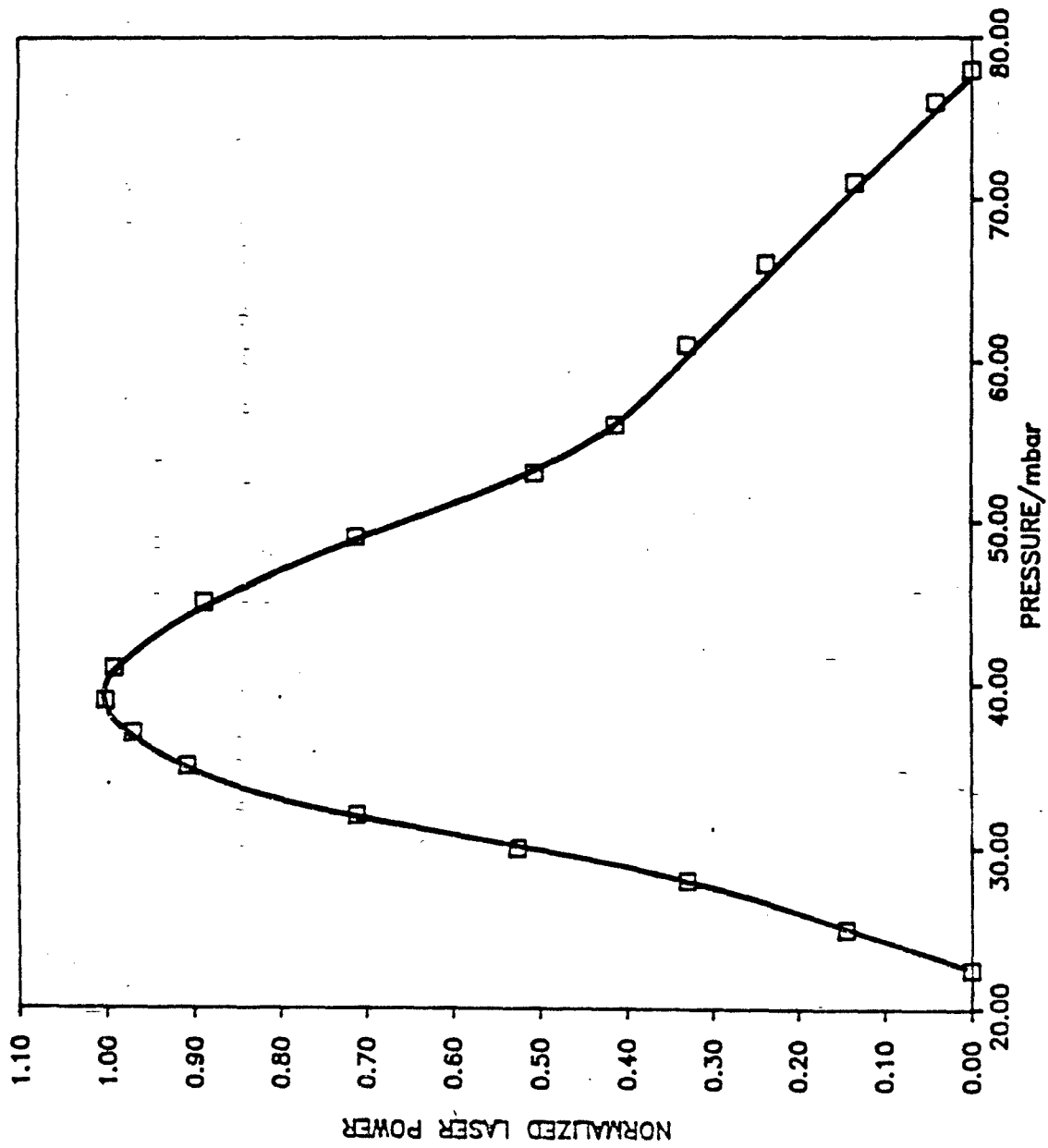


Fig. 4 Normalized laser power versus pressure in the mixing volume at otherwise optimum conditions.

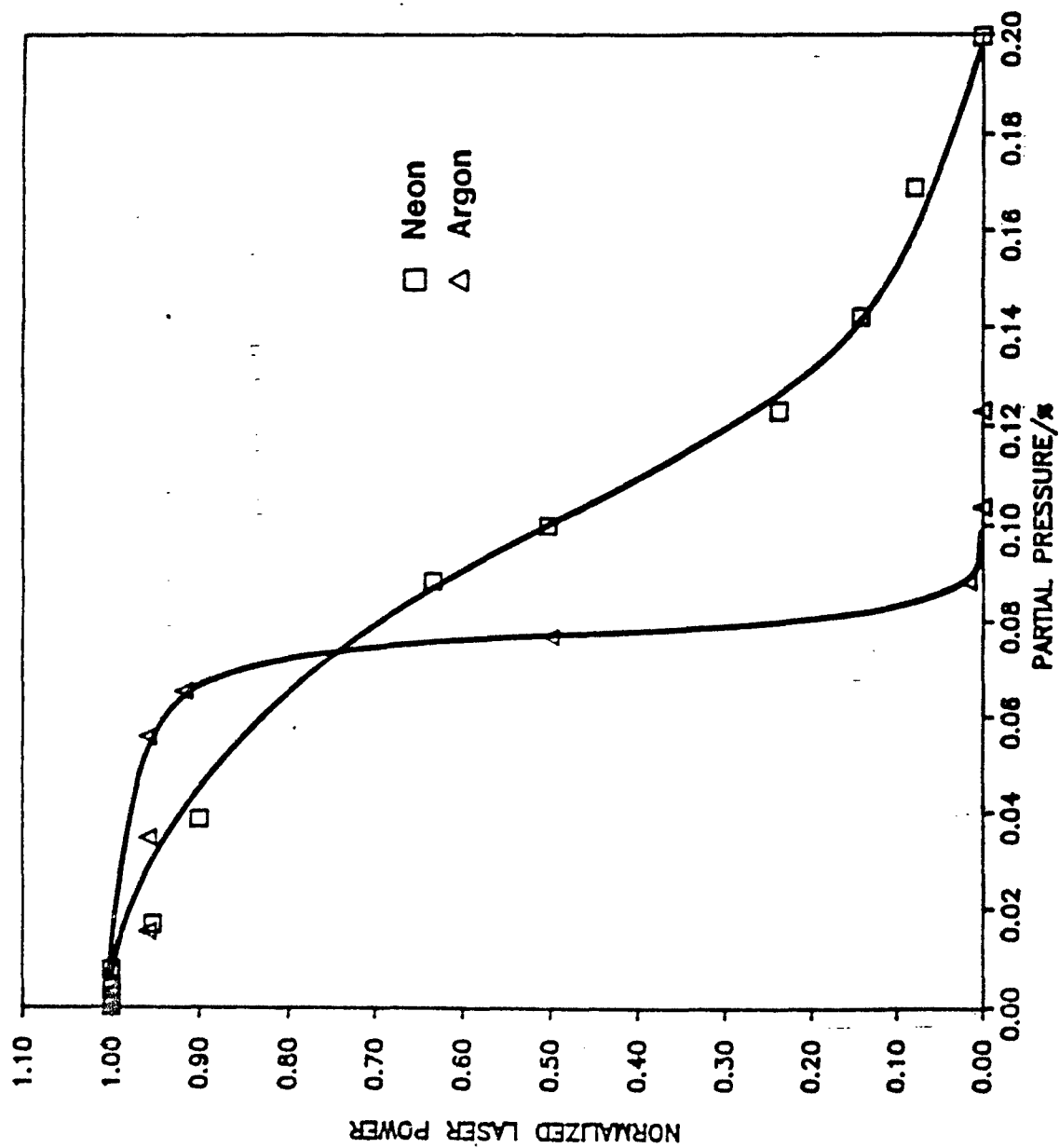


Fig. 5 Normalized laser power versus the fraction of neon or argon to helium in the plasma source.

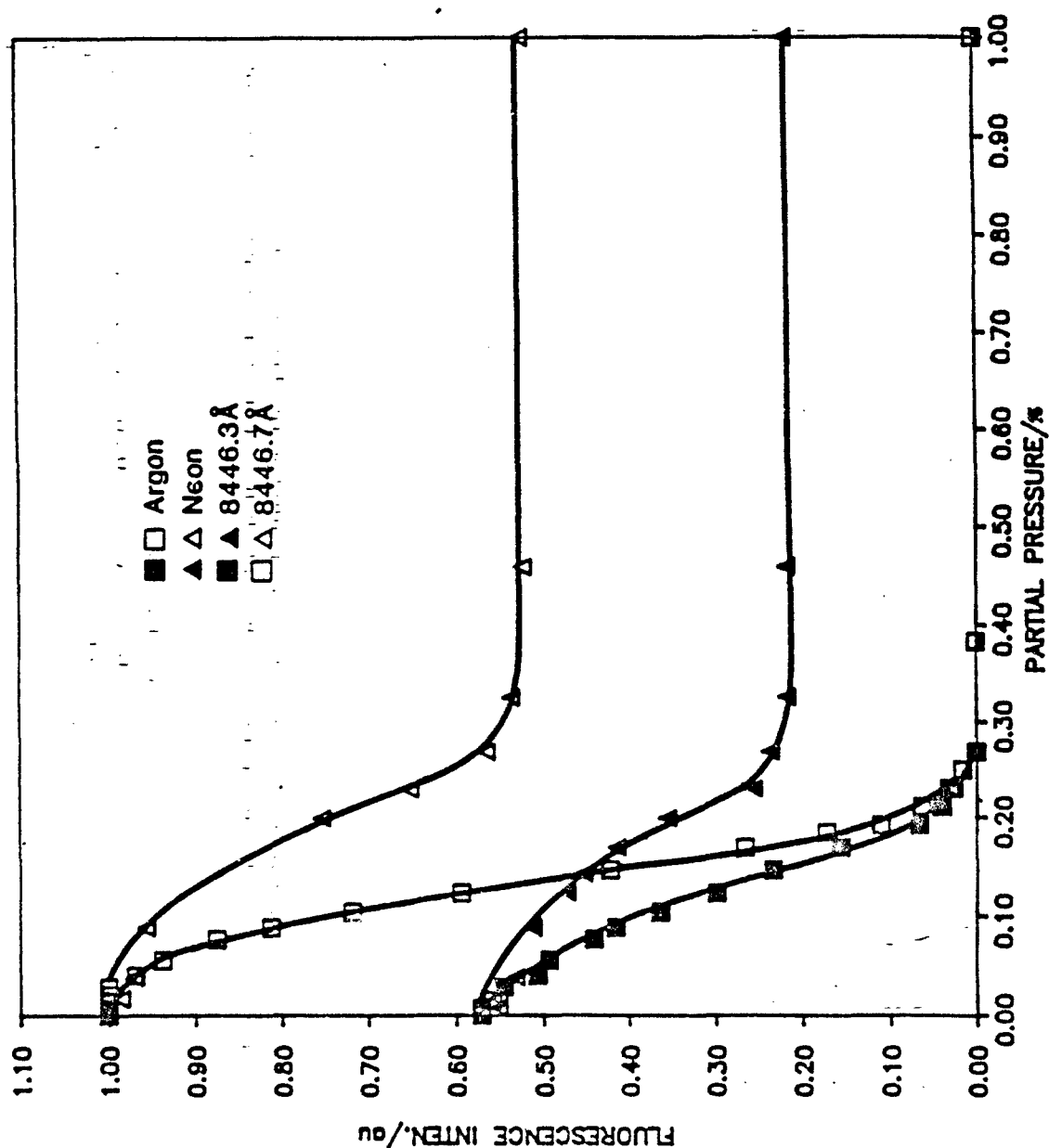


Fig. 6 Normalized fluorescence intensity of two laser lines versus the fraction of neon or argon to helium in the plasma source.

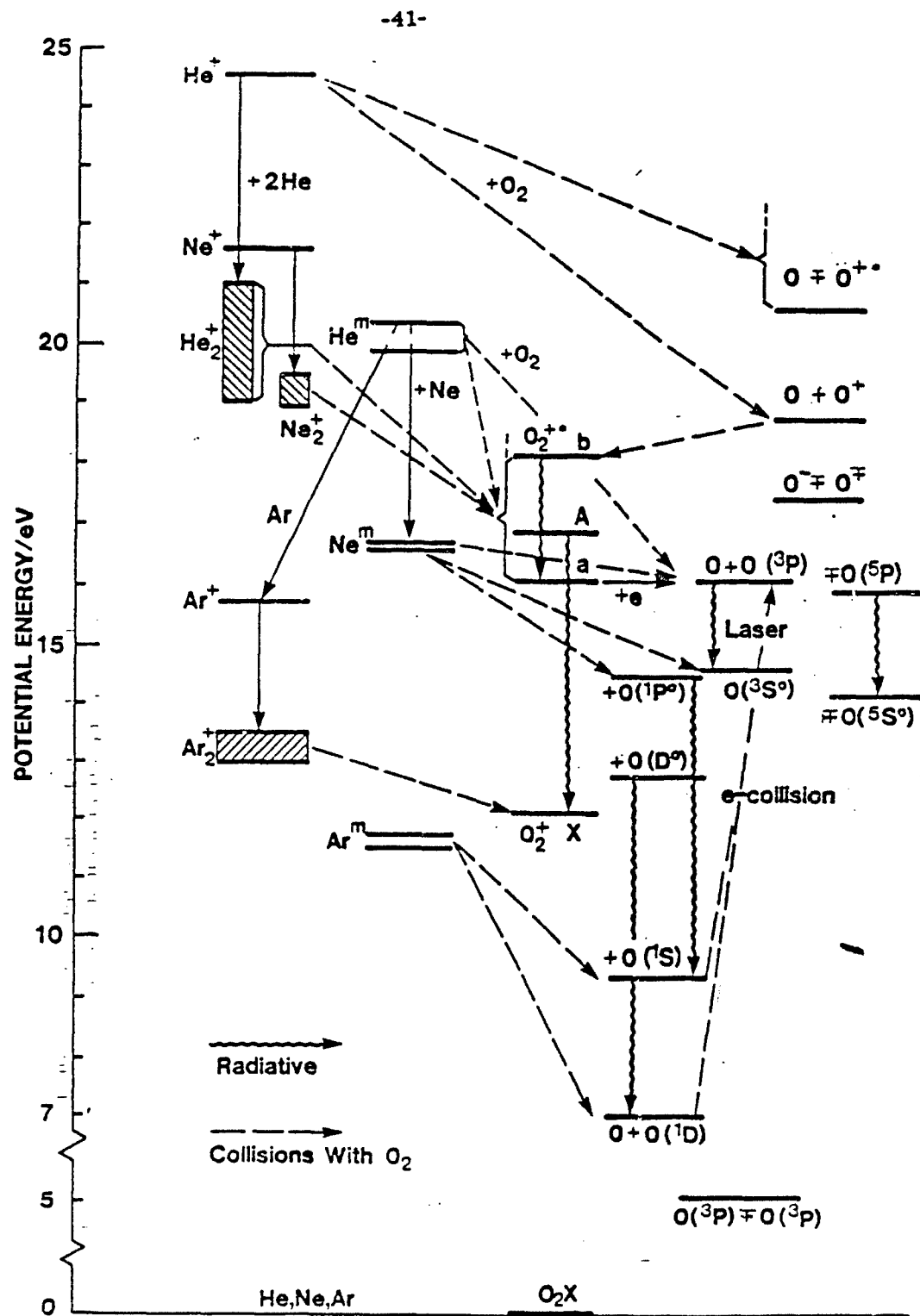


Fig. 7 Energy level diagram and processes contributing to the excitation mechanism of the atomic oxygen lasers.

# On the Excitation Mechanism of the CW Atomic Fluorine Laser

GERHARD SCHAEFER, SENIOR MEMBER, IEEE, AND HULYA KIRKICI, MEMBER, IEEE

**Abstract**—A plasma mixing device in which a helium plasma beam is crossed with a molecular fluorine beam was used to operate an atomic fluorine laser. Operation conditions confirm that excitation occurs through collisions of helium metastables and  $F_2$  molecules. Collisions with other F-donors such as  $NF_3$ ,  $CF_4$ ,  $C_2F_6$ , and  $SF_6$  do not yield F-atoms in one of the possible upper laser levels. In lasers using such F-donors, excitation has to occur through electron collisions with F-atoms which have been generated in a preceding process.

## I. INTRODUCTION

RESONANT or near-resonant energy transfer from metastable rare-gas atoms to other species has, from the beginning of gas laser development, been recognized as an ideal mechanism to generate population inversions for laser action in the near-IR, visible, and near-UV spectral regimes [1]. The major advantage of this mechanism is that only a small number of states (the upper laser states) are excited and that essentially no atoms are directly excited into the lower laser states.

The disadvantage of this mechanism comes from the fact that the metastable atoms have to be produced first and that at the same time a sufficient density of collision partners in the ground state has to be maintained. This is usually accomplished either in an externally-sustained plasma or in a gas discharge in a mixture of a rare gas in which with metastables are produced, and a second gas to which the energy transfer process into highly-excited states takes place. This second gas, therefore, has energy states with excitation cross sections with much lower threshold energies than the rare gas. If the plasma is sustained by an external-high-energy electron beam, then the efficiency of producing metastable rare-gas atoms only depends on the values of the cross sections at high energies, and not on the differences in the threshold energy. In a gas discharge, however, the low-energy electrons generated through ionization have to be accelerated in the gas before they can excite, and subsequently, they lose their energy again in the inelastic (and elastic) collisions. Excitation of the atoms with the lower excitation threshold therefore has a much higher probability.

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An additional advantage can be gained by utilizing near-resonant energy transfer collisions between metastable rare-gas atoms and molecules. The quantum efficiency in molecular systems can be much higher because of the high density of low-lying vibrational and rotational states in the electronic ground state, which can act as the lower laser states. However, two disadvantages result from using molecules. The first disadvantage is that near-resonant energy transfer now can lead to a large number of energy states or even into a band, and consequently the gain of the laser is lower. This problem does not occur if the molecules are excited into a repulsive branch and dissociate into fragments, one of which is an excited atom. In this case, of course, the advantage of a possible high quantum efficiency is also lost. The other disadvantage is that the high density of low-lying states in molecules makes it nearly impossible to generate metastable rare-gas atoms efficiently in gas discharges unless the fraction of the molecular gas is very low ( $\leq 10^{-3}$ ).

As an alternative excitation method for utilizing resonant energy transfer from metastable rare-gas atoms to molecules we, therefore, proposed to use fast plasma mixing of two beams, one of which contained metastable rare-gas atoms at high densities, and the other one containing the molecular species [2].

Besides the advantages mentioned above, this method also provides some insight into the excitation mechanisms of lasers excited by energy transfer collisions. In a gas discharge other mechanisms compete based on the direct interaction of fast electrons with the molecular gas. Such processes may not play a significant role if the plasma generation is well separated from the mixing regime, where the excitation through energy transfer occurs.

The following sections present experimental results on the CW laser action in atomic fluorine in the red and near-IR spectral regime. The experiments were performed using a fast plasma mixing device. The interpretation of these results leads to a better understanding of the possible excitation mechanisms of the atomic fluorine laser. It also provides further information on the efficiency and the branching ratio of the energy transfer collisions between helium metastables and  $F_2$ .

## II. EXPERIMENTAL RESULTS

The experimental setup has been described earlier [2] and is only briefly summarized. Two beams are generated by two slit nozzles under an angle of  $90^\circ$ , directly adja-

cent to each other (Fig. 1). The slit widths were typically 100  $\mu\text{m}$  and the length was 2 cm in the direction perpendicular to Fig. 1. One slit acted as a hollow cathode with an upstream anode to produce the helium plasma beam. The other slit was used to generate a beam of the molecular gas with helium as a buffer gas.

All of the experiments were performed with helium as a feed gas for the plasma source (nozzle 1) and a mixture of 5 percent  $\text{F}_2$  in helium was flowed through nozzle 2. If no gas was flowed through nozzle 2, a plasma jet was observed with visible emission (blue, as typical for helium) over at least 2 cm length in flow direction. When  $\text{F}_2$  (5 percent  $\text{F}_2$  in a buffer of He) was flowed through nozzle 2 this visible afterglow disappeared and a bright red emission appeared in the mixing zone, a narrow regime close to the two nozzles. Experimental investigations were performed on the fluorescence, emitted from the mixing zone and on the laser emission depending on the system parameters such as the input pressure of nozzle 1 (the plasma source)  $p_1$ , the input pressure of nozzle 2 (a molecular gas)  $p_2$ , the outlet pressure in the mixing volume  $p_{\text{out}}$ , and the current and voltage of the hollow cathode discharge. These parameters were kept at the optimum operating conditions for maximum laser power ( $p_1 = 490$ ,  $p_2 = 300$ , and  $p_{\text{out}} = 65$  mbar;  $I = 1$  A;  $V = 220$  V) unless indicated otherwise.

The measurements of the fluorescence intensities of the emitted fluorine lines give information on the branching ratio of the energy transfer collisions. Wavelengths and transitions were taken from [4]. An important question is whether the  $3p$  states are populated directly through energy transfer collisions or radiative from higher-lying states. The near-IR transitions  $4s-3p$  and  $3d-3p$  were not accessible with our monochromator. Transitions from any higher lying F-state were not observed. For reasons discussed in the section on the excitation mechanism we assume that the  $3p$ -states are mainly excited directly.

The intensities can be converted into transition rates and all rates originating from the same upper level can be added to evaluate the branching ratio for the excitation of the individual  $3p$ -states, as shown in Table I for 3 different pressures in the mixing zone and otherwise optimum conditions.  $p_{\text{out}} = 5$  mbar was the lowest pressure at which we could operate the hollow cathode over the full length. For  $p_{\text{out}} \geq 20$  mbar the branching ratio depends only weakly on the pressure in the mixing zone. A possible explanation for the pressure dependence is that the ratio of the densities of the two helium metastables ( $^3S_1$ ,  $^1S_0$ ) changes with pressure. Table I shows that at pressures above 13 mbar, more than 50 percent of the collisions yield quartet states with approximately 25 percent into  $^4P_{3/2}$ . The lower levels of the quartet transitions,  $3s$   $^4P_{1/2,3/2,5/2}$  are metastable and can only be quenched collisionally. Continuous laser action of quartet lines at low pressure is therefore not expected.

The doublet states with the high excitation rates are  $^2P_{1/2}$ ,  $^2P_{3/2}$ , and  $^2S_{1/2}$  with approximately 10 percent each. The lower doublet levels decay fast through radi-

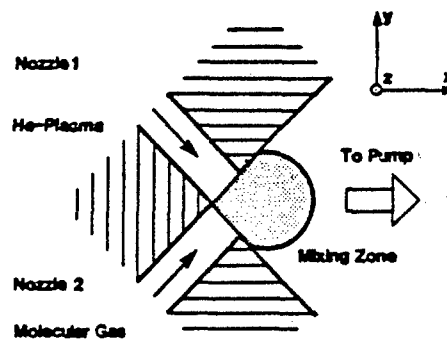


Fig. 1. Geometry of 2-beam plasma mixing device.

TABLE I  
BRANCHING RATIO FOR THE EXCITATION OF FLUORINE ATOMS IN COLLISION  
OF HELIUM METASTABLES AND FLUORINE MOLECULES AT DIFFERENT  
PRESSURES

State	Energy (eV)	Branching Ratio at $p_{\text{out}} =$		
		5 mbar	13 mbar	31 mbar
$^2P_{1/2}^o$	14.76	15.7	13.1	12.5
$^2P_{3/2}^o$	14.75	26.0	13.9	10.5
$^2S_{1/2}^o$	14.68	9.4	11.5	11.6
$^2D_{3/2}^o$	14.61	3.4	3.1	2.6
$^2D_{5/2}^o$	14.58	3.2	2.6	1.8
Total Doublet		57.7	44.2	39.0
$^4S_{3/2}^o$	14.68	1.7	1.8	2.2
$^4D_{3/2}^o$	14.55	1.5	4.7	6.0
$^4D_{5/2}^o$	14.54	5.7	8.6	11.3
$^4D_{7/2}^o$	14.53	2.6	1.8	1.5
$^4D_{9/2}^o$	14.50	6.7	3.7	3.2
$^4P_{1/2}^o$	14.40	6.2	5.1	4.4
$^4P_{3/2}^o$	14.39	8.1	7.5	5.2
$^4P_{5/2}^o$	14.37	9.8	22.6	27.2
Total Quartet		42.3	55.8	61.0

ative transitions. Resonance radiation trapping could, in general, limit the depletion of the  $3s$ -levels; however, in a volume as small as in our device (see below) and at low pressure, this seems to be unlikely. We also did not observe a decrease of the laser output in the center of the gain profile as observed previously, which is considered to be the consequence of resonance absorption of the lower laser level in combination with an excitation mechanism generating atoms in the upper laser level with high velocity [20].

The dependence of the fluorescence intensity of one doublet and one quartet line on hollow cathode current are shown in Fig. 2. All lines show the same saturation behavior which is the same as the known saturation of the metastable density with current in hollow cathode discharges [3]. At low currents ( $< 0.4$  A) only part of the cathode is active, causing fluctuations of the emission intensity.

The extension of the emission from the mixing zone was measured in the horizontal and vertical directions ( $x$  and  $y$  directions in Fig. 1). Fig. 3 shows the profile of the

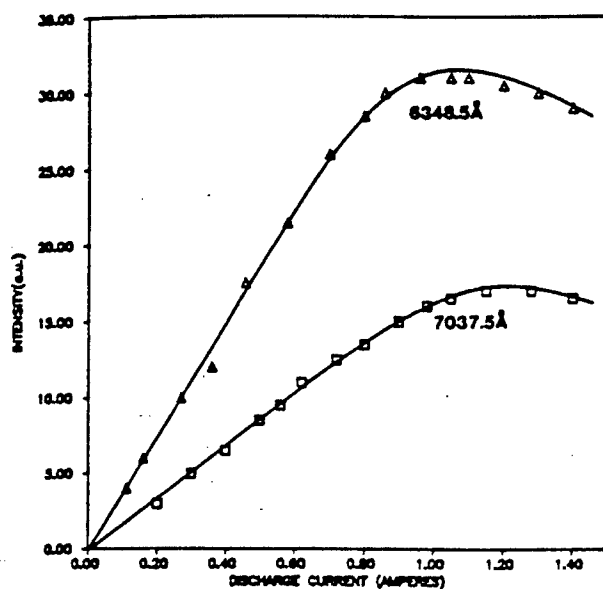


Fig. 2. Fluorescence intensity versus hollow cathode current for one doublet line (7037.5 Å) and one quartet line (6348.5 Å).

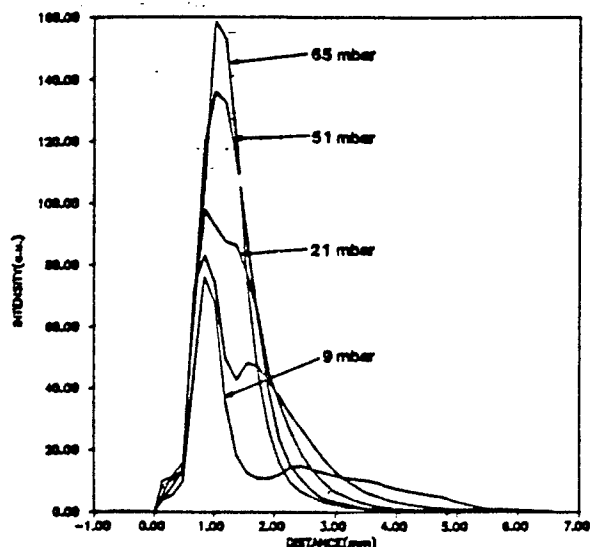


Fig. 3. Intensity profile in the  $x$  direction (see Fig. 1) of the 7037.5 Å emission from the mixing zone.

mixing zone in the  $x$  direction for the laser line,  $\lambda = 7311$  Å. The variable parameter is the outlet pressure in the mixing volume  $p_{out}$ , at otherwise optimum conditions for the gas flow through the two nozzles. A similar profile is found for the  $y$  direction. The maximum intensity was achieved at an outlet pressure of  $\sim 65$  mbar, which is also the optimum condition for laser action. Considering that the slit length is 2 cm we find that under these conditions the active volume is a column of approximately 0.5 mm in diameter and 2 cm long. For too-low outlet pressures, the mixing volume obviously increases and for too-high pressures, complete mixing of the two beams is no longer accomplished.

TABLE II  
DOUBLET TRANSITIONS, WAVELENGTHS, AND  
EINSTEIN COEFFICIENTS

Transition	$\lambda$ (Å)	$A_{ul}$ ( $10^8 s^{-1}$ )
$^2P_{1/2} - ^2P_{3/2}$	6966	0.160
$^2P_{1/2}$	7128*	0.294
$^2P_{3/2} - ^2P_{1/2}$	7037*	0.38
$^2P_{1/2}$	7202	0.072
$^2S_{1/2} - ^2P_{3/2}$	7311*	0.27
$^2P_{1/2}$	7489	0.13
$^2D_{3/2} - ^2P_{3/2}$	7607	0.061
$^2P_{1/2}$	7800	0.29
$^2D_{3/2} - ^2P_{3/2}$	7755	0.35

\*CW laser operation.

For the laser experiments, a near-concentric resonator with a beam waist diameter of less than 100  $\mu m$  was aligned through the mixing zone with its axis perpendicular to the plane shown in Fig. 1. As previously reported, laser action was possible over a wide range of operation parameters [2]. Of special importance for the interpretation of the excitation mechanism is the large outlet pressure range for laser action (at  $I = 1$  A and  $2 \text{ mbar} \leq p_{out} \leq 310 \text{ mbar}$ ).

Continuous laser action was observed on lines 7037, 7128, and 7311 Å (see Table II). The upper levels of these lines are the doublet states with the highest pump rates (see Table I), and the laser transitions from these states are the ones with the highest transition probabilities [5], [6]. Since the active region of the laser was only 2 cm long, a resonator was used with highly-reflecting mirrors. It is therefore expected that the laser line with the lower threshold will limit the population of the upper laser level such that no other laser line starting from the same level will oscillate. With a laser line discriminating resonator it should also be possible to achieve continuous laser operation on other doublet transitions starting from the same upper levels.

Fig. 4 shows the power dependence of all laser lines depending on current, showing essentially the same saturation behavior as the fluorescence. Fig. 5 shows the maximum laser intensity depending on outlet pressure  $p_{out}$ . The optimum conditions are the same as the one found for the fluorescence intensity (compare Fig. 3).

From the resonator losses at laser threshold and the fluorescence intensities at threshold and at maximum power we estimated the maximum gain for each line considering that resonance radiation trapping does not influence the population of the lower laser level:  $g_m(7037 \text{ Å}) = 0.89$  percent/cm;  $g_m(7128 \text{ Å}) = 0.91$  percent/cm;  $g_m(7311 \text{ Å}) = 0.75$  percent/cm. These estimates are conservative since only mirror transmission losses have been considered.

We also performed experiments with other molecular gases containing fluorine, such as  $NF_3$ ,  $CF_4$ ,  $C_2F_6$ , and  $SF_6$ . If one of these gases was flowed through nozzle 2 the helium afterglow also disappeared, indicating quench-

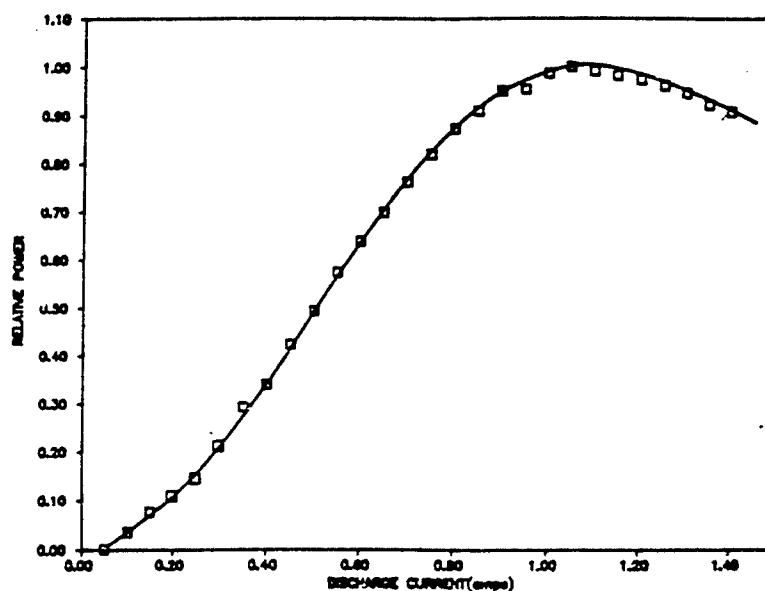


Fig. 4. Laser power versus hollow cathode current for all three laser lines (7037.5, 7127.9, and 7202.4 Å) at otherwise optimum conditions (see text).

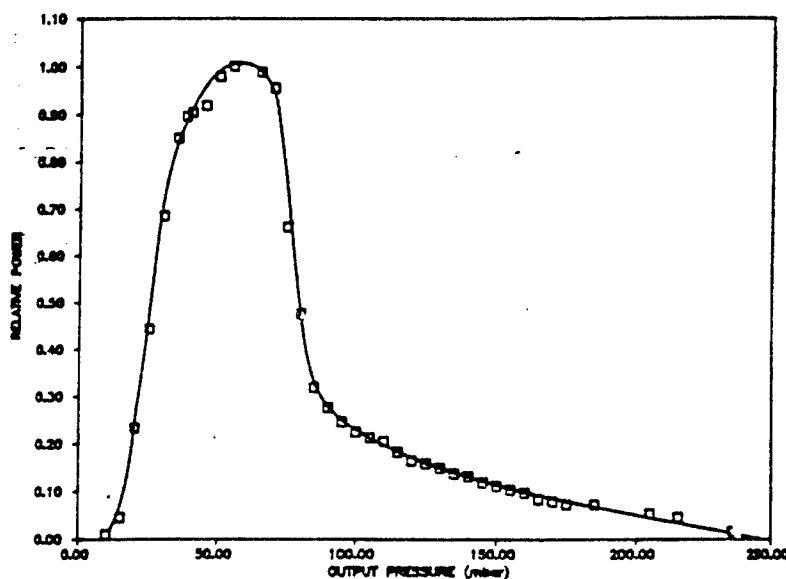


Fig. 5. Laser power versus output pressure at otherwise optimum conditions (see text).

ing of the helium metastables; however, no fluorescence on any of the red or near-IR lines shown in Table I was observed.

### III. THE EXCITATION MECHANISM

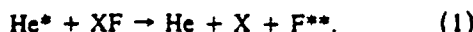
Laser action in atomic fluorine was first reported in pulsed discharges in  $\text{SF}_6$  [7]. Since then, fluorine lasers have been operated in a variety of pulsed-gas discharge devices. Helium was in all cases the major fraction of the gas mixture and F-donors such as  $\text{F}_2$ ,  $\text{HF}$ ,  $\text{NF}_3$ ,  $\text{CF}_4$ ,

$\text{C}_2\text{F}_6$ ,  $\text{PF}_5$ ,  $\text{SF}_6$ , and  $\text{AgF}$  have been used [8]–[19]. Continuous fluorine laser operation has only been achieved with electron-beam pumping [20] and fast plasma mixing [2].

Many different excitation mechanisms have been proposed and it seems likely that atomic fluorine can be excited in different ways. The following presents a list of processes which have been proposed as excitation mechanisms for the atomic fluorine laser. XF represents one of the mentioned F-donors.

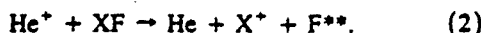


**Energy Transfer Collisions:** These were first considered for He-HF mixtures [9]:

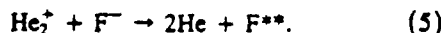
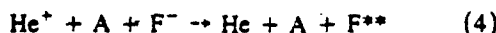


Hocker concluded from spectroscopic investigations on He-F<sub>2</sub> mixtures that this process proceeds via the intermediate dissociative state of HeF [13].

**Charge Exchange Collisions** [17], [19]:



**Ion-Ion Recombination** [14], [20]:



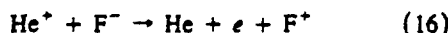
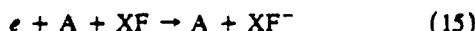
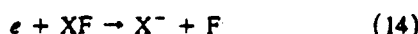
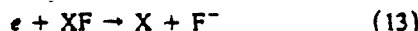
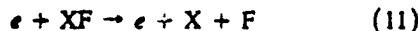
**Recombination** [14], [20]:



**Electron Collision Excitation:**



**For Processes Involving Fluorine Atoms or Ions:** These have to be produced in a preceding process [21], [22]:



The probability for one of these collisions to occur is proportional to the product of the densities of the collision partners and a rate constant for the specific process. The rate constants for collisions involving electrons strongly depend on the electron-energy distribution. Excitation and ionization cross sections have thresholds at higher energies than the attachment processes. In our plasma mixing device, the F-donors are injected into the flowing afterglow of a hollow cathode discharge where the mean electron energy is low. Exciting or ionizing collisions of electrons with F-donors will therefore not occur.

From our experimental results we can draw the following conclusions on the excitation mechanism of the atomic fluorine laser.

1) The dependence of laser power and fluorescence intensity on hollow cathode current indicates that resonant energy transfer from helium metastables is the dominant

excitation mechanism in fast plasma mixing devices with F<sub>2</sub> as the F-donor [(1)].

2) The same current dependence also indicates that collisions between helium ions and F<sub>2</sub> do not significantly contribute to the excitation of F-atoms [(2)-(5)], [16], [17]. The fact that this current dependence was independent of pressure in a wide pressure range suggests that neither He<sup>+</sup> nor He<sub>2</sub><sup>+</sup> have to be considered. The presence of He<sub>2</sub><sup>+</sup> was confirmed by using N<sub>2</sub> as a molecular gas. Strong emission of radiation from N<sub>2</sub><sup>+</sup> was observed.

3) The fact that in our plasma mixing device the molecular gas is injected into the plasma behind a flowing hollow cathode suggests that electrons are slow and electron collisions with energetic electrons do not contribute in our experiment [(7), (8)]. This can also be concluded from the wide pressure range in which laser operation was possible [2].

4) The experiments with other F-donors clarify that near-resonant energy transfer collisions of helium metastables with NF<sub>3</sub>, CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and SF<sub>6</sub> yielding excited F-atoms in 3p-states do not exist. Since the quenching rates of helium metastables through these molecules is known to be large [14], we have to assume that either molecular states are excited or dissociation occurs yielding F-atoms either in the ground state or excited into the lower states of the laser transition (3s). All these F-donors also generate F<sup>-</sup> ions confirming that ion-ion recombination processes do not contribute to the excitation mechanism [(3)-(5)].

5) Since other laser systems have been operated with F-donors which do not allow one to generate excited F-states directly, we have to conclude that F-atoms are produced first, either through dissociation [(11)], attachment [(13)-(15)], or ion-ion recombination [(16), (17)]. Excitation occurs through collisions with fast electrons. The role of helium metastable here is restricted to the generation of atomic fluorine. Excitation with fast electrons is, besides excitation through energy-transfer collisions, the only mechanism which we cannot exclude to be a possible excitation mechanism since in our experiment fast electrons do not reach the mixing zone where excitation occurs. We therefore conclude that in fluorine lasers operating with the above-mentioned F-donors, atomic fluorine is produced first and then excited through electron collisions.

6) In pulsed discharge and electron-beam pumping of gas mixtures of helium and fluorine both mechanisms, energy transfers from helium metastables to F<sub>2</sub> and electronic excitation of F-atoms may occur at the same time.

#### ACKNOWLEDGMENT

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## APPENDIX IV

### Charge Transfer Collisions between $\text{He}_2^+$ Ions and $\text{N}_2$ : Branching Ratio into Vibrational States.

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#### Abstract

A plasma mixing device in which a helium plasma beam is crossed with a molecular nitrogen beam was used to measure the branching ratio of the excitation of individual vibrational levels of the  $\text{B}^2\Sigma$  electronic state of the molecular nitrogen ion in charge transfer collisions between  $\text{He}_2^+$  ions and ground state  $\text{N}_2$  molecules. The branching ratio of the excitation of individual vibrational levels of the  $\text{C}^3\Pi$  electronic state of the neutral nitrogen molecule due to the resonant energy transfer collisions between argon metastables and ground state nitrogen molecules was also measured using a plasma beam of a mixture of argon and helium. These results allow comparison of our measurements with results obtained using other techniques.

## Introduction

Resonant charge and energy transfer collisions between atomic or molecular ions and ground state molecules have been recognized as efficient pumping mechanisms to generate population inversion in gas lasers due to the high selectivity of these types of collisions. One example in which the pump mechanism is charge transfer is the nitrogen ion laser.

The first laser oscillation in the first negative system of the nitrogen ion has been reported by Collins [1,2] in mixtures of He+N<sub>2</sub> excited by a fast pulsed electron beam, and by Ishchenko [3] in a fast transverse discharge. Since then several attempts have been made to increase the output power [4] and the overall efficiency [5] of the nitrogen ion laser. Pulsed laser action occurred on the three transitions from the  $v''=0$  vibrational level of the B<sup>2</sup>Σ electronic state to the  $v'=0,1,2$  vibrational levels of the X<sup>2</sup>Σ ground state of the molecular nitrogen ion. Collins [1] proposed that resonant charge transfer collision between molecular helium ions and ground state nitrogen molecules is the main pumping mechanism with an efficiency of the process approaching unity. The branching ratio into individual vibrational levels of the B<sup>2</sup>Σ electronic state of the nitrogen ion has not been reported. The energy difference between the vibrational levels of the B<sup>2</sup>Σ state is approximately ~0.3eV. Because the charge transfer collision between He<sub>2</sub><sup>+</sup> ions and N<sub>2</sub> molecules is a resonant type of process, excess energy provided by vibrationally excited He<sub>2</sub><sup>+</sup> ions would be expected to appear as the population of vibrationally excited states of N<sub>2</sub><sup>+</sup>(B). On the other hand, after the charge transfer process collisional relaxation of the higher vibrational states will further populate the  $v''=0$  state. Therefore, in order to obtain the net branching ratio of the excitation into individual vibrational states, the device has to operate at lower pressure to avoid collisional relaxation. However, at lower pressures, the production of He<sub>2</sub><sup>+</sup> is

not efficient and  $\text{He}^+$  is the dominant ion. Furthermore,  $\text{He}^+$  is resonant with the  $v''=3$  vibrational level of the  $\text{C}^2\Sigma$  electronic state of the nitrogen ion. In order to avoid this resonant charge transfer process between  $\text{He}^+$  and  $\text{N}_2$ ,  $\text{He}_2^+$  has to be produced efficiently; at the same time the collisional relaxation contribution to the excitation of  $v''=0$  has to be kept to a minimum. This is possible if the generation of  $\text{He}_2^+$ -ions and the charge transfer processes are performed separately.

In this work we will present experimental results of the branching ratio for the excitation of individual vibrational levels of the  $\text{B}^2\Sigma$  of  $\text{N}_2^+$  by collisions with  $\text{He}_2^+$  performed using a fast plasma mixing device. Molecular ions are produced in a flowing hollow cathode discharge at higher pressures the ground state nitrogen molecules are then injected into the expanding afterglow at low pressures. Intensity measurements of the emission of the  $(\text{B}^2\Sigma)$  to  $(\text{X}^2\Sigma)$  transitions at different pressures and the extrapolation of these values to zero pressure provide the branching ratio.

### Experimental Setup

In recent papers [8,9] the experimental setup was described and the possibility of using a plasma mixing device to utilize near resonant energy transfer collision between metastable atoms and ground state molecules to generate the population inversion was discussed. Therefore, the experimental setup is only briefly explained in this paper. Two beams are generated by two perpendicular slit nozzles, each with a cross section of typically  $0.1 \text{ mm} \times 20 \text{ mm}$ . The mixing occurs at the junction of the beams generated by these slits (see Fig. 1). One beam is the flowing afterglow of a hollow cathode discharge operated with helium or a mixture of helium and argon. The other beam is pure nitrogen. The mapping of the fluorescence profile of the mixing zone

showed that the volume of the active regime is approximately 0.5 mm in diameter and 20 mm in length [10]. Experimental investigations were performed on the fluorescence emitted from the mixing zone on the system parameters such as the input pressure,  $p_1$ , of nozzle 1 which is the plasma source, the input pressure,  $p_2$ , of nozzle 2 which is the molecular gas, nitrogen, the outlet pressure,  $p_{out}$ , in the mixing volume and current  $I$  and voltage  $V$  of the hollow cathode discharge. After the optimum intensity of the (0-0) transition of first negative system was reached, the following operating parameters were kept constant:  $p_1=510$  mbar,  $p_2=220$  mbar,  $I=1.0$  A,  $V=200$  V; only the pressure in the mixing zone,  $p_{out}$  was varied.

In the plasma mixing device the main energy carriers which reach the mixing volume are the long living species such as metastables and ions. Fast electrons are also generated due to collisions between metastable atoms. As discussed in a previous paper [10], generation of fast electrons is interrupted when the molecular gas is injected into the flowing afterglow. Since the hollow cathode discharge is operated at pressures well above 100 mbar, one expects a fast generation of  $\text{He}_2^+$  molecular ions due to three-body collisions of  $\text{He}^+$  with He atoms.

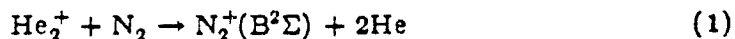
### Experimental Results

Our spectroscopic investigation of the emitted light in the spectral region between 200 nm and 900 nm showed three molecular band systems: the first negative system of the molecular nitrogen ion with an intensity of over 80% of the total fluorescence intensity, an unidentified IR band system, and the second positive system of the neutral nitrogen molecule with an intensity of less than 1.0% of the total fluorescence intensity. No other molecular or atomic lines belonging to either helium or nitrogen were detected.

The wavelengths of the most intense band heads of the system in the IR region are  $\lambda=782\text{ nm}$ ,  $\lambda=855\text{ nm}$ . The appearance of this system is very similar to the first negative system of the nitrogen ion. Also, the intensity dependence of the  $\lambda=782\text{ nm}$ -line on the hollow cathode discharge current (Fig. 2) shows the same behavior as the intensity dependence of the (0-0) transition of the first negative system at  $\lambda=391.4\text{ nm}$  which is distinctly different from that of the (0-0) transition of the second positive system of  $\text{N}_2$  at  $\lambda=337.1\text{ nm}$ . Therefore, we conclude that these lines also belong to an ionic system of the nitrogen molecule. At this time we do not know the exact transition or the excitation mechanism of these lines.

The weak emission of the second positive system of neutral nitrogen was directly proportional to the pressure in the mixing volume. Since there are no energetic electrons or other energy carriers that can excite ground state nitrogen molecules to the  $\text{C}^3\Pi$  state, we conclude that these lines are the result of recombination processes of molecular nitrogen ions leading to the excited states of the neutral nitrogen molecule.

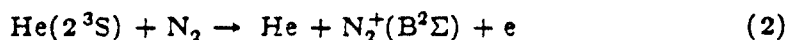
Very intense emissions from the  $(\text{B}^2\Sigma; v'') \rightarrow (\text{X}^2\Sigma; v')$  transitions of the molecular nitrogen ion was observed with over 80% of the total fluorescence intensity. Excitation is accomplished through the charge transfer process



with a rate coefficient of  $k=1.1 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$  [11]. Vibrational states excited in the fast plasma mixing device are  $v''=0,1,2,3$ . Sensitivity of our equipment allow us to detect any transition which has intensity of greater than 0.01%. Under this condition, no transition originating from a vibrational state  $v''=4$  or higher was observed.

Measurements of the fluorescence intensities of the ( $B^2\Sigma; v''$ ) to ( $X^2\Sigma; v'$ ) lines gave information on the branching ratio of the charge transfer collision into the vibrational states  $N_2^+(B^2\Sigma)$ . Intensities can be converted into transition rates and all rates originating from the same upper level can be added to evaluate the excitation rates of individual vibrational states. These rates have been measured for different pressures in the mixing zone (see Fig. 3). Extrapolation of the fitted curves to zero pressure gives the branching ratios for the excitation of the individual vibrational states: 92.71% into  $v''=0$ , 7.18% into  $v''=1$ , 0.10% into  $v''=2$  and 0.01% into  $v''=3$ .

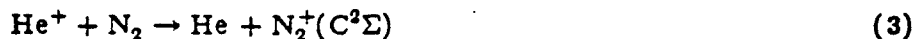
As seen in Fig. 3, at higher pressures collisional relaxation of the excited nitrogen molecule ( $v''>0$ ) to the ( $v''=0$ ) caused an increase in the (0-n) transitions and a decrease in the other ( $v''=1,2-n$ ) transitions. However, the branching ratio of the  $v''=3$  state increased with increasing outlet pressure. We assume that Penning ionization [11,12] between helium metastables contributes to the excitation of the  $v''=3$  state.



with a rate coefficient of  $k=7.8 \times 10^{-11} \text{cm}^3 \text{sec}^{-1}$  [11]. Even though the branching ratio of reaction (2) is high [11], the rate of the reaction is 2 orders of magnitude smaller than the rate of charge transfer process (reaction 1); therefore, Penning ionization does not significantly contribute to the excitation of the  $B^2\Sigma$  state.

Resonant charge transfer between atomic helium ions and ground state nitrogen molecules is the main excitation mechanism of the second negative system of the nitrogen ion in helium-nitrogen discharges at low pressures ( $< 1$  torr) [14].

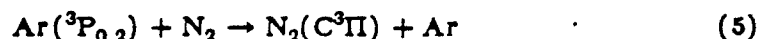




According to the extensive study of reaction (3) by T.R. Govers et al. [13], the branching ratio leading into the  $\text{C}^2\Sigma$  states is over 60% with 85% excitation to the  $v''=3$  vibrational level. However, in our experimental investigation we did not observe any transition originating from  $\text{N}_2^+(\text{C}^2\Sigma)$ . We therefore conclude that most of the  $\text{He}^+$  ions are converted into  $\text{He}_2^+$  ions before they reach the reaction volume.

#### Comparison with Other Experimental Methods

To compare our experimental results with data obtained with different experimental methods, we also investigated the resonant energy transfer collisions between argon metastables and ground state nitrogen molecules.



For this process, the branching ratio into the individual vibrational levels has been measured previously by Bochkova et al. [15] by using rf-discharge excitation. For the branching ratio measurements, the hollow cathode in our plasma mixing device was operated with a mixture of 33% Ar and 67% He. The second positive system of nitrogen ( $\text{C}^3\Pi \rightarrow \text{B}^3\Pi$ ) was the only observed emission. Therefore, we conclude that argon metastables are the only energy carrier species that can transfer energy to nitrogen, causing excitation of the  $\text{C}^3\Pi$  electronic state in the mixing volume. Figure 4 shows again the dependence of the branching ratios of the excitation into individual vibrational levels of the  $\text{C}^3\Pi$  electronic state of  $\text{N}_2$  on the outlet pressure,  $p_{\text{out}}$ , in the mixing zone. The extrapolation of the fitted curves to  $p_{\text{out}}=0$  yielded the branching ratio for the excitation into individual vibrational states: 74.8% into  $v''=0$ , 20.3% into  $v''=1$ , 4.3% into  $v''=2$ , and 0.6% into  $v''=3$ . The results given

by Bochkova et al. [15] are: 74.% into  $v''=0$ , 20.1% into  $v''=1$ , 4.3% into  $v''=2$ , 1.0% into  $v''=3$  and 0.4% into  $v''=4$ .

### Conclusion

A plasma mixing device where the molecular helium ions are produced at high pressures and ground state nitrogen molecules crossed at low pressures was used to study the charge transfer between  $\text{He}^+$  and  $\text{N}_2$ . The branching ratio of excitation of individual vibrational levels of  $\text{C}_2\Sigma$  was measured.

The branching ratio results presented in this work showed that over 92% of the charge transfer is into the  $v''=0$  vibrational level of the  $\text{B}^2\Sigma$  electronic state of nitrogen ion, and only less than 8% is into  $v''=1, 2$ , and 3. Furthermore, we undertook a comparison of our work on the branching ratios of excitation of  $\text{C}^3\Pi$  electronic state with other techniques and obtained consistent results. Therefore, we conclude that such a device used in our experimental measurements is a candidate for the operation of the CW nitrogen ion laser at wide operating pressure range.

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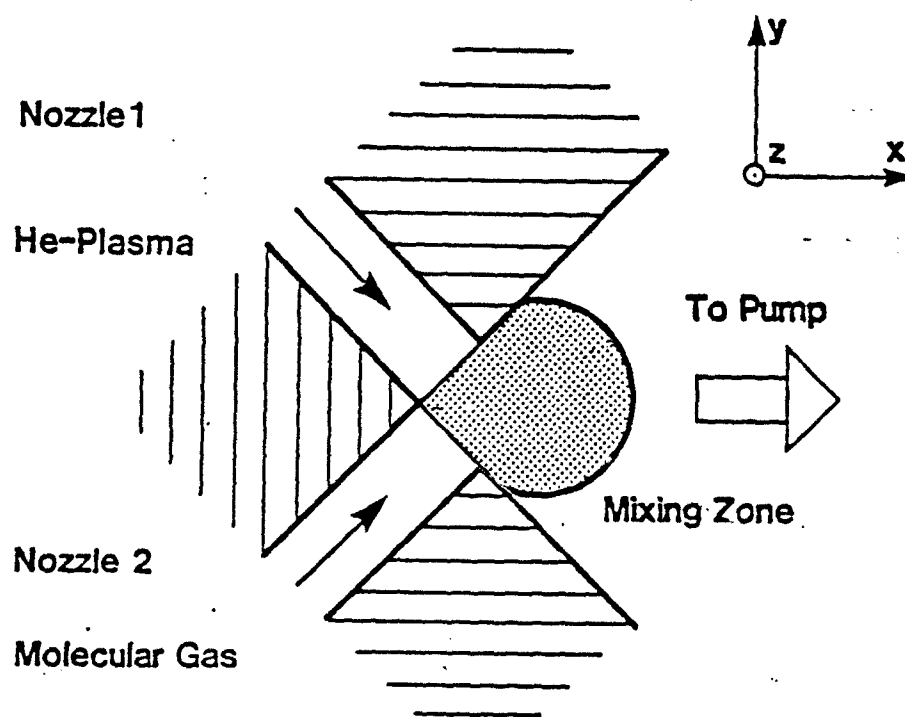


Fig. 1 Geometry of a 2-beam plasma mixing device

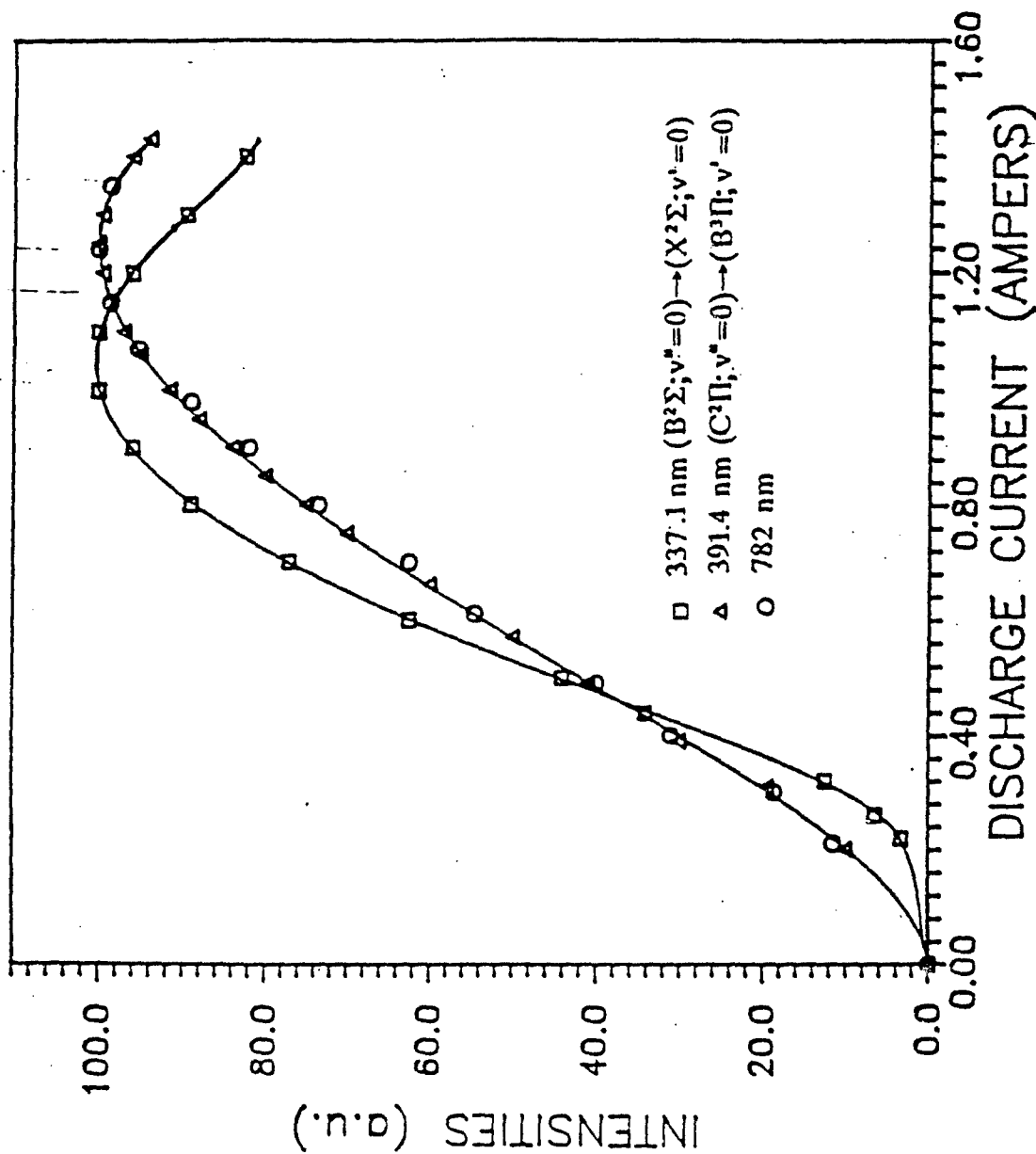


Fig. 2 Normalized fluorescence intensities vs. hollow cathode current at otherwise optimum conditions ( $p_1=510$  mbar,  $p_2=220$  mbar,  $p_{out}=20$  mbar and  $V=200$  Volts).

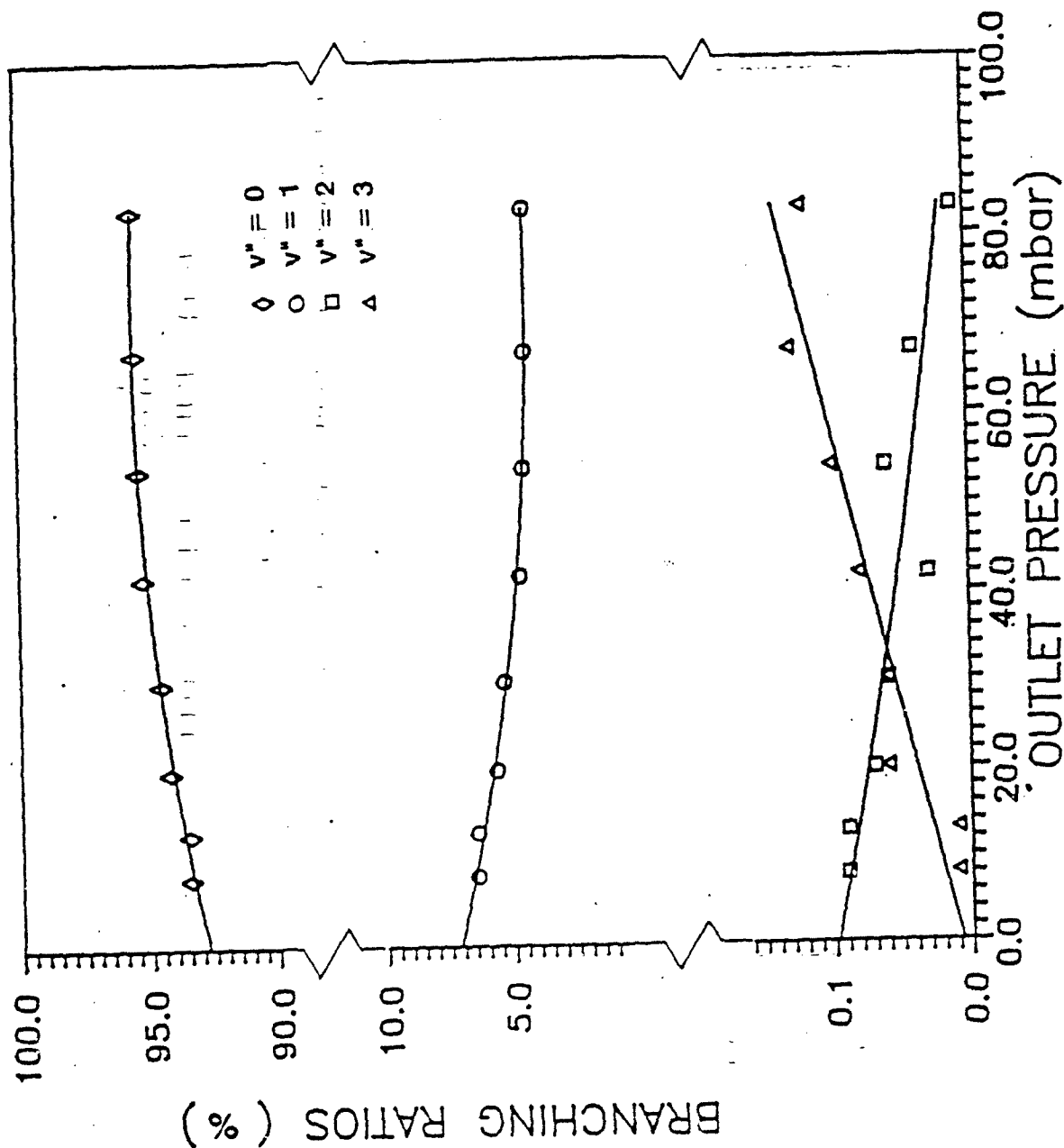


Fig. 3 Branching ratios of the  $B^2\Sigma$  state of  $N_2^+$  vs. outlet pressure at otherwise optimum conditions ( $p_1=510$  mbar,  $p_2=220$  mbar,  $I=1.0$  A and  $V=200$  Volts).

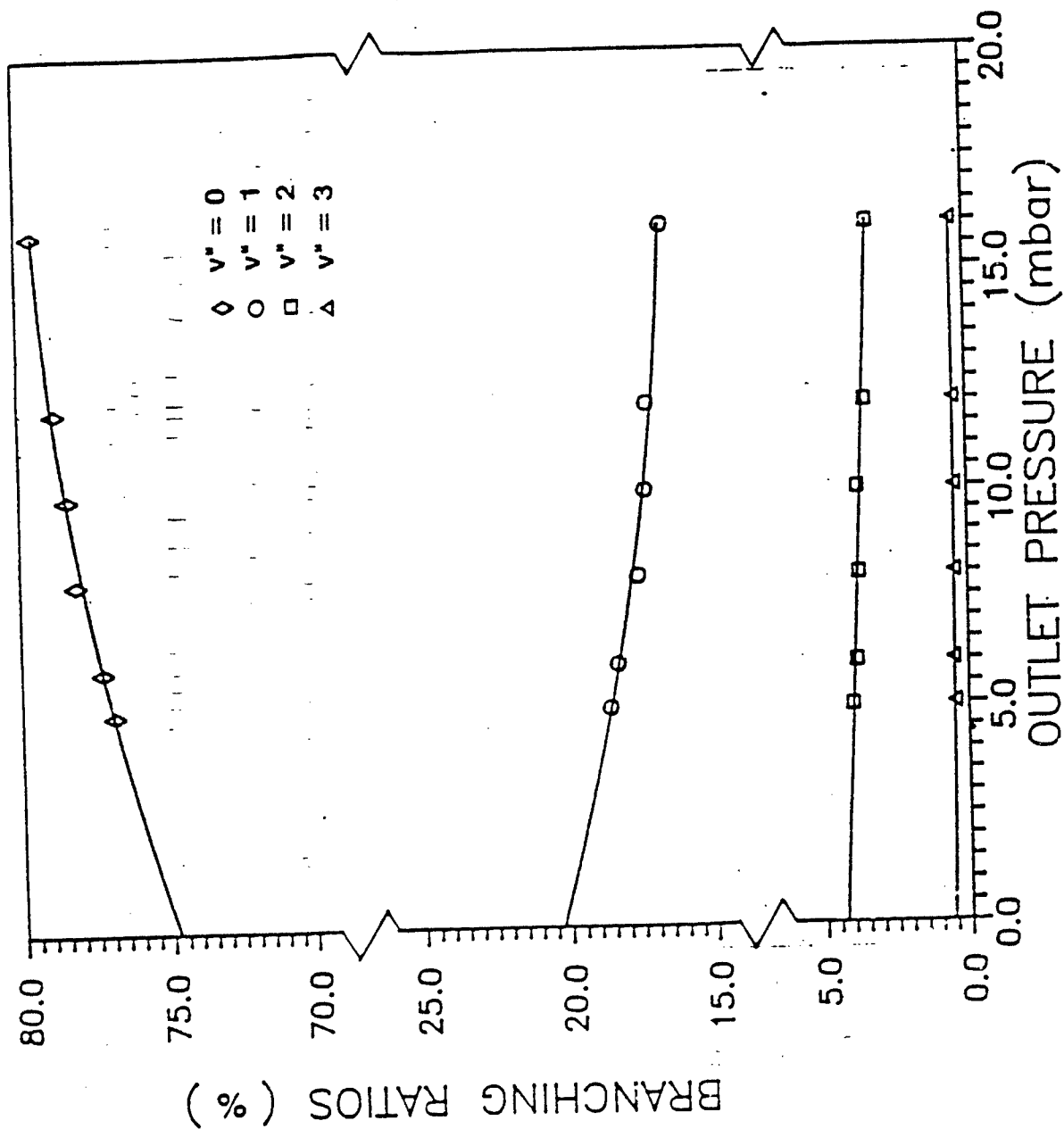


Fig. 4 Branching ratios of the  $C^3\Pi$  state of  $N_2$  vs. outlet pressure. Operating

conditions are  $p_1 = 470$  mbar,  $p_2 = 350$  mbar,  $I = 1.0$  A, and  $V = 220$  V.